

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:			

United States Patent and Trademark Office (Box PCT) Crystal Plaza 2 Washington, DC 20231 ETATS-UNIS D'AMERIQUE

Date of mailing (day/month/year) 01 May 1997 (01.05.97)	in its capacity as elected Office
International application No. PCT/NL96/00362	Applicant's or agent's file reference PCT 0501
International filing date (day/month/year) 16 September 1996 (16.09.96)	Priority date (day/month/year) 15 September 1995 (15.09.95)
Applicant	
VAN KESSEL, Louis, Peter, Marie et al	

1.	The designated Office is hereby notified of its election made:
	X in the demand filed with the International Preliminary Examining Authority on:
	08 April 1997 (08.04.97)
	in a notice effecting later election filed with the International Bureau on:
2.	The election X was
	was not
	made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland

Authorized officer

Céline Faust

Telephone No.: (41-22) 730.91.11

Facsimile No.: (41-22) 740.14.35



PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	FOR FURTHER ACTION	see Notification of (Form PCT/ISA/2	Transmittal of International Search Report (20) as well as, where applicable, item 5 below.
PCT 0501 International application No.	International filing date(lavimonthiyear)	(Earliest) Priority Date (day, month, year)
PCT/NL 96/ 00362	16/09/19	,	15/09/1995
Applicant			
ROERMOND PAPIER B.V. et a	1.		
This International Search Report has bee according to Article 18. A copy is being	n prepared by this Internat transmitted to the Internation	ional Searching Aut onal Bureau.	hority and is transmitted to the applicant
This International Search Report consists It is also accompanied by a cop	s of a total of 3 by of each prior art docume	sheets. nt cited in this repo	· C
1. Certain claims were found unsea	archable (see Box I).		
2. Unity of invention is lacking (se	e Box II).		
3. The international application of international search was carried	ontains disclosure of a mucle d out on the basis of the sec	eotide and/or amino quence listing	acid sequence listing and the
· file	d with the international app	lication.	
fur	nished by the applicant sep	arately from the inte	rnational application,
	but not accompanied matter going beyond	by a statement to the the disclosure in the	ne effect that it did not include international application as filed.
Tr:	anscribed by this Authority		
1	e text is approved as submit e text has been established b		•
i the	e text uss oeen established t	y uns Addionty to	Table as renovin
5. With regard to the abstract,	e text is approved as submi	tted by the applicant	_
	has been actablished	according to Rule 3	R 2(h), by this Authority as it appears in
80	ox III. The applicant may, the committee on the committee of the committee on the committee of the committee	within one month tr	om the date of maining of diff intermedia-
6. The figure of the drawings to be pu	blished with the abstract is:		_
	suggested by the applicant		X None of the figures.
be	cause the applicant failed to		••
be	cause this figure better cha	racterizes the invent	on.

Form PCT/ISA/210 (first sheet) (July 1992)

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 D21H17/02 D21H17/22

D21H17/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) IPC 6 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

ategory *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Κ	US 5 011 741 A (HOFFMAN ROGER P) 30 April	1,4-6
4	1991 see the whole document	9,10
×	EP 0 546 956 A (GOMEZ DANIEL ;TECH DU PAPIER CENTRE (FR)) 16 June 1993 see claims 2,3	1,4,5,9
(US 3 166 466 A (PUYDAK) 19 January 1965 see claim 1	1-3
x	US 1 755 744 A (MUNKTELL) 22 April 1930 see the whole document	1,2
X	BE 331 525 A (ANTOINE) 29 January 1926 see the whole document	1,2
	-/	

X Further documents are listed in the continuation of box C.	X Patent family members are listed in annex.
*Special categories of cited documents: 'A' document defining the general state of the art which is not considered to be of particular relevance. 'E' earlier document but published on or after the international filing date. 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified). 'O' document referring to an oral disclosure, use, exhibition or other means. 'P' document published prior to the international filing date but later than the priority date claimed.	T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention 'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone 'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is considered to involve an inventive step when the document, such combined with one or more other such documents, such combination being obvious to a person skilled in the art. '&' document member of the same patent family
Date of the actual completion of the international search	Date of mailing of the international search report
9 January 1997	11.07.97
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patendaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo ni, Fax: (+ 31-70) 340-3016	Authorized officer Songy, 0

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Internation No 96/00362

C.(Continuat	on) DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 659 997 A (WENZEL) 13 May 1938 see the whole document	1,2
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NTER TIONAL SEARCH REPORT

n on patent family member

revenue la Application No CT/NL 96/00362

AU-A- 7351891 26-09-9 CA-A- 2038638 21-09-9 DE-D- 69104249 03-11-9 DE-T- 69104249 16-03-9 EP-A- 0448344 25-09-9 JP-A- 4214497 05-08-9 US-A-3166466 19-01-65 NONE US-A-1755744 22-04-30 NONE BE-A-331525 NONE	Patent document cited in search report	Publication date	Paten men	Publication date		
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DE-A-659997 NONE	BE-A-331525		NONE			
	DE-A-659997		NONE			



REQUEST

For realing Office use only	
International Application No.	
International Filing Date	
Name of receiving Office and "PCT International Application"	

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty. Applicant's or agent's file reference PCT 0501 (if desired) (12 characters maximum) Box No. I TITLE OF INVENTION Paper and cardboard comprising starch- and protein-containing material Box No. II APPLICANT (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) This person is also inventor. Roermond Papier B.V. Telephone No. Mijnheerkensweg 18 6041 TA Roermond Facsimile No. the Netherlands Teleprinter No. State (i.e. country) of nationality: State (i.e. country) of residence: NL This person is applicant all designated all designated States except the United States of America the United States the States indicated in X for the purposes of: of America only the Supplemental Box FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S) Box No. III (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) Name and address: This person is: van Kessel, Louis Peter Marie applicant only Ursulahof 58 5995 CG Kessel applicant and inventor the Netherlands inventor only (If this check-box is marked, do not fill in below.) State (i.e. country) of nationality: State (i.e. country) of residence: NT. NT. This person is applicant all designated States except the United States of America all designated the United States the States indicated in x for the purposes of: States of America only the Supplemental Box Further applicants and/or (further) inventors are indicated on a continuation sheet. Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE The person identified below is hereby/has been appointed to act on behalf agent common representative of the applicant(s) before the competent International Authorities as: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) Telephone No. 070 - 3500464 Smulders, Th.A.H.J.,c.s. c/o VEREENIGDE OCTROOIBUREAUX Facsimile No. Nieuwe Parklaan 97 070 - 3522723 2587 BN The Haque Teleprinter No. the Netherlands

Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to

indicate a special address to which correspondence should be sent. PCT/RO/101 (first sheet) (5 July 1994; reprint July 1996)

Continuation of Box No. III FURTHER APPLICANTS AND/OR (FURTHER) INVENTORS						
If none of the jumping sub-boxes is used, this sheet is not to be including the request.						
Name and address: (Family name followed by given name; for designation: The address must include postar Kuypers, Gerardus Henricus Andre Cornelishoflaan 3 6042 ND Roermond the Netherlands	This person is:					
State (i.e. country) of nationality:	State (i.e. country) of residence:					
This person is applicant all designated all designated for the purposes of:	the United States except States of America. **The United States of the States indicated in the Supplemental Box					
Name and address: (Family name followed by given name: fo designation. The address must include postar Maessen, Matheus Petrus Marie van Hövellstraat 35 5988 AG Helden the Netherlands	This person is: applicant only applicant and inventor inventor only (If this check-bax is marked, do not fill in below.)					
State (i.e. country) of nationality:	State (i.e. country) of residence:					
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This person is applicant all designated all designated for the purposes of:	ted States except States of America					
Further applicants and/or (further) inventors are indicated	on another continuation sheet.					

Form PCT/RO/101 (continuation sheet) (July 1993; reprint July 1996)

See Notes to the request form

Box No	o.V	DESIGNATION OF	ITES			
The fo	llowi	ng designations are hereby n	nade under Ruie 4.9(a	(mark t	he ap	plicable check-baxes; at least one must be marked):
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The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation of a designation consists of the filling of a notice specifying that designation and the payment of the designation and confirmation fuez. Confirmation must reach the receiving Office within the 15-month time limit.)

Box No. VI PRIORITY CLAIM Further priority claims are ted in the Supplemental Box						
The priority of the following earlier application(s) is hereby claimed:						
Country (in which, or for which, the application was filed)	Filing Date (day/month/year)	Application No.	Office of filing (only for regional or international application)			
item (1). NL	15. 09. 1995 15 september 1995	1001218				
item (2)						
item (3)	•					
application is the receiving Office	certified copy of the earlier application is a (a fee may be required): nereby requested to prepare and transport the earlier application(s) identified	,	poses of the present international			
BOX NO. VIE INTERNATIO	NAL SEARCHING AUTHORITY	E .				
are competent to carry out the inter Earlier search Fill in where a se out orrequested and the Authority.	ching Authority (ISA) (If two or mornational search, indicate the Authority charch (international, international-type or is now requested to base the international eference to the relevant application (or the Date (day/month/year): 03 May 1996	osen; the two-letter code may be used);] other) by the International Searching Au search, to the extent possible, on the resu	thority has already been carried its of that earlier search. Identify the search request:			
Box No. VIII CHECK LIST	<u>r</u>					
the following number of she 1. request : 4 2. description : 19 3. claims : 2 4. abstract : 1 5. drawings : 2 Total : 26	sheets	f attorney general f attorney f attorney 6. separa deposi nt explaining signature 7. nucleo sequer document(s) d in Bax No. VI 8. other (culation sheet te indications concerning ited microorganisms ptide and/or amino acid ace listing (diskette) (specify):			
Figure No of the	drawings (if any) should accompany	y the abstract when it is published.				
Box No. IX SIGNATURE OF APPLICANT OR AGENT Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request). H. A. M. Marsman						
	For receiving C	Office use only				
Date of actual receipt of the international application:	· ·		2. Drawings:			
 Corrected date of actual rec timely received papers or de the purported international 	rawings completing		received:			
Date of timely receipt of the corrections under PCT Arti	cie í 1(2):		not received:			
International Searching Aut specified by the applicant:	hority ISA / 6. (Transmittal of search copy de until search fee is paid	layed			
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Date of receipt of the record or by the International Bureau:	рру					

Form PCT/RO/101 (last sheet) (January 1994; reprint July 1996)

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See Notes to the request form

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REQUEST

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The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty. Applicant's or agent's file reference the second secon (if desired) (12 characters maximum) PCT 0501 Box No. I TITLE OF INVENTION Paper and cardboard comprising starch- and protein-containing material Box No. II APPLICANT (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) Name and address: This person is also inventor. Roermond Papier B.V. Telephone No. Mijnheerkensweg 18 6041 TA Roermond the Netherlands Facsimile No. Teleprinter No. State (i.e. country) of nationality: State (i.e. country) of residence: NLThis person is applicant all designated States all designated States except the United States of America the United States the States indicated in the Supplemental Box X for the purposes of: of America only FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S) Box No. III Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) This person is: van Kessel, Louis Peter Marie applicant only Ursulahof 58 5995 CG Kessel applicant and inventor the Netherlands inventor only (If this check-box is marked, do not fill in below.) State (i.e. country) of nationality: State (i.e. country) of residence: NLNL This person is applicant all designated States all designated States except the United States of America the United States the States indicated in for the purposes of: x of America only the Supplemental Box Further applicants and/or (further) inventors are indicated on a continuation sheet. Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: agent common representative (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) Name and address: Telephone No. 070 - 3500464 Smulders, Th.A.H.J., c.s. □/○ VEREENIGDE OCTROOIBUREAUX Facsimile No. Nieuwe Parklaan 97 070 - 3522723 2587 BN The Hague the Netherlands Teleprinter No. Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Sheet No 2	PCI/AL 16/30362							
Continuation of Box No. III FU ER APPLICANTS AND/OR (FURTHER) INV	ORS							
If none of the following sub-boxes is used, this sheet is not to be included in the request.								
Name and address: (Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country.) Kuypers, Gerardus Henricus Andreas Cornelishoflaan 3 6042 ND Roermond the Netherlands	This person is: applicant only applicant and inventor inventor only (If this check-box is marked, do not fill in below.)							
State (i.e. country) of nationality: NL State (i.e. country) of re	sidence:							
This person is applicant all designated all designated States except for the purposes of: All designated the United States of America X Of America X	United States the States indicated in the Supplemental Box							
Name and address: (Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country.) Maessen, Matheus Petrus Marie van Hövellstraat 35 5988 AG Helden the Netherlands	This person is: applicant only applicant and inventor inventor only (If this check-box is marked, do not fill in below.)							
	NL United States the States indicated in							
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)	This person is: applicant only applicant and inventor inventor only (If this check-box is marked, do not fill in below.)							
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Further applicants and/or (further) inventors are indicated on another continuation shee	et.							

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Box ?	Y.oV	DESIGNATION OF STATES								
The fe	oilow	ing designations are hereby made under Rule 4.9(a)	mark	the ap	pplicable check-boxes; at least one must be marked):					
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X	AP	ARIPO Patent: KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SZ Swaziland, UG Uganda, and any other State which is a Contracting State of the Harare Protocol and of the PCT.								
X	EA	Eurasian: Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT.								
X	EP	European Patent: AT Austria; BE Belgium; CH and LI Switzerland and Liechtenstein, DE Germany, DK Denmark, ES Spain, FI Finland, FR France; GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT								
X	OA	OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)								
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In addition to the designations made above, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except the designation(s) of

The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation of a designation consists of the filling of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)

	-	Sheet No.	4					
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Titel: Papier en karton omvattende zetmeel- en eiwithoudend materiaal

De uitvinding is gelegen op het gebied van de papieren kartonfabricage. In het bijzonder betreft de uitvinding de toepassing van een combinatie van zetmeel- en eiwithoudend materiaal in papier en karton. Overigens wordt in deze beschrijving en de conclusies onder de term "papier" mede karton begrepen.

Van oudsher worden zetmelen op grote schaal en in grote volumina toegepast in de papier- en kartonindustrie. Bij de productie van gecoat papier, dat in hoofdzaak als grafisch papier in de fijnpapierindustrie wordt toegepast, wordt het onder andere als bindmiddel in de strijklaag toegepast. Dit zetmeel is over het algemeen een gemodificeerd zetmeel.

Daarnaast wordt zetmeel gebruikt als toeslagstof om de sterkte-eigenschappen, en met name de droog-sterkte-eigenschappen, van het papier te verbeteren. Daartoe worden conventioneel in de papierindustrie gebruikte zetmelen en anionogene en kationogene derivaten van deze zetmelen aangewend, waarvoor bijvoorbeeld kan worden verwezen naar EP-A-0 545 228 en WO-A-94/05855.

In dit verband kan verder worden verwezen naar Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition (1981), John Wiley & Sons, Volume 16, blz. 803 en verder, in het bijzonder blz. 814-819.

In de meest gangbare toepassingen van zetmeel als vezelversterkende component wordt het ofwel - veelal in de vorm van kationogeen zetmeel - in het natte gedeelte van het papierproces in de massa van het papier gebracht, ofwel - in hoofdzaak in de vorm van oplosbaar gemaakt natief zetmeel - door middel van de zogenaamde lijmpers in de papiervezelmassa geïmpregneerd.

Deze bekende sterkte-verbeterende additieven geven voordelen, zowel in economische als in technische c.q. technologische zin; zij geven het papier of het karton een toegevoegde waarde. Naast het verschaffen van een toegevoegde

waarde in gebruikelijke papier- en kartonprocessen, maakt in het bijzonder het toenemende gebruik van zwakkere vezels, steeds vaker hergebruikt oud papier, alsmede een steeds verdere toename van vulstoffen in plaats van vezels in dit oud papier met als gevolg een afnemend sterkte-potentieel, en de afnemende beschikbaarheid van sterke, langvezelige bestanddelen in de basispulp voor papier, de behoefte aan additieven voor het verhogen van de sterkte groot.

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Overigens wordt thans reeds benadrukt dat de uitvinding niet beperkt is tot "waste-based" papier. De uitvinding strekt zich uit over het hele gebied van de papier- en kartonfabricage, inclusief papier op "virgin fibre" basis.

De bekende additieven op basis van zetmeel kunnen op grote schaal interacties aangaan met de cellulosegroepen van papiervezels. Aldus ontstaat een vergroting van het aantal bindingen tussen de papiervezels onderling, wat de vezelvezel-binding versterkt en daarmee de sterkte-eigenschappen van het eindproduct verbetert.

In conventionele processen waarin zetmelen als 20 sterktemiddel worden toegepast, worden strenge eisen gesteld aan het eiwitgehalte dat in het toegepaste zetmeelproduct aanwezig mag zijn. In het bijzonder wordt bij de papierfabricage ingezet natief zetmeel, in hoofdzaak natief tarwe-, mais- of aardappelzetmeel, aangeleverd met een extra 25 specificatie voor maximale eiwitgehalten van 0,3-0,5 gew.%, betrokken op de droge stof. Hogere eiwitgehalten worden geacht als verontreiniging te werken en klontervorming en afzettingen in het systeem te veroorzaken. Zo leidt het dispergeren van gluten (de eiwitfractie in tarwebloem) tot klontering en 30 schuimvorming. Deze nadelen treden in versterkte mate op wanneer deze eiwitten in het papiervervaardigingsproces aan hogere temperaturen worden blootgesteld.

Het zetmeel dat de basisgrondstof vormt voor de thans gebruikte zetmeeladditieven in papier, wordt gewonnen uit een groot aantal plantaardige bronnen, bijvoorbeeld uit graankorrels, zoals tarwe, mais en rijst; uit knollen, zoals aardappelen en tapioca; of uit andere plantendelen, zoals sago.

Uit de voornoemde plantaardige bronnen wordt het zetmeel onder toepassing van een combinatie van mechanische stappen, zuiveringsstappen en droogstappen vrijgemaakt. De afgescheiden eiwithoudende fracties, alsmede andere bijproductfracties worden afgevoerd. Bij de zetmeelzuivering komen veel afvalstromen vrij, zoals biologisch materiaal houdende waterstromen. Deze stromen vormen meer en meer een milieuprobleem, waardoor lozing zonder meer niet meer mogelijk is.

De bereiding van het zetmeel dat in de grootste hoeveelheden in de papierindustrie wordt toegepast als vezelversterkend en papierverstijvend middel, te weten tarwezetmeel, wordt als voorbeeld beschreven. Soortgelijke processen worden uitgevoerd om zetmeel uit andere plantaardige bronnen voor de papierindustrie toepasbaar te maken.

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komen.

Tarwekorrels bestaan hoofdzakelijk uit twee bestanddelen. De kern, het zogenaamde endosperm, bestaat voor het grootste gedeelte uit zetmeel en eiwit. De buitenlaag, de zemelen of het kaf, bevat voornamelijk cellulose. De verhouding kern:buitenlaag bedraagt ongeveer 80:20.

Deze tarwekorrels worden gemalen, waarbij het kaf van de kern wordt gescheiden. Het afgescheiden endosperm, dat voor ongeveer 70-80% uit zetmeel en voor ongeveer 10-15% uit eiwit bestaat, wordt gebruikelijk aangeduid met de term "bloem". Afhankelijk van de uitmalingsgraad van het tarwe wordt meer of minder zuivere bloem verkregen. Zo wordt bij een uitmalingsgraad van ongeveer 80% "grauwe bloem" verkregen, terwijl bij een wat lagere uitmalingsgraad van circa 70% aanmerkelijk zuiverder bloem wordt verkregen, omdat bij deze uitmalingsgraad geen delen anders dan de endosperm in de bloem

Bij de productie van zetmeel voor de papierindustrie wordt vervolgens het eiwit, met name de gluten, uit de bloem gewassen. De bloem wordt aldus in de twee hoofdcomponenten gescheiden. Zoals reeds is aangegeven worden bij dit proces economisch onrendabele droogstappen uitgevoerd, kan een deel van de uitgangsstof tarwe niet worden gebruikt en worden afvalstromen gecreëerd die moeten worden verwerkt.

Het primaire doel van de onderhavige uitvinding is te voorzien in een werkwijze waarbij een geoptimaliseerd gebruik wordt gemaakt van grondstoffen in die zin dat een zo groot mogelijke fractie van de grondstof in het papierproces kan worden ingezet.

Dit doel wordt bereikt door de bestanddelen van bloem volledig in het vervaardigingsproces van papier of karton in te brengen, zonder dat deze bloem of bloembestanddelen vooraf worden gemodificeerd door er kationogene of anionogene groepen aan te binden of dergelijke eiwit/zetmeelmengsels vooraf droog worden gemodificeerd. Met andere woorden wordt het doel bereikt door uit te gaan van natieve eiwit/zetmeelmengsels en die als zodanig toe te passen. Onder "bloem" wordt in deze beschrijving en conclusies wordt verstaan een eiwit- en zetmeelbevattende fractie die uit een en dezelfde plantaardige bron afkomstig is, ofwel een natuurlijk mengsel van eiwit en zetmeel.

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Meer in het bijzonder betreft de uitvinding papier of karton omvattende de bestanddelen van natieve bloem in de papiervezelmatrix. Daarnaast betreft de uitvinding een werkwijze voor het vervaardigen van papier of karton, waarbij bloem in hoofdzaak wordt onderworpen aan een zetmeel en eiwit oplosbaar makende behandeling waarna de behandelde bestanddelen van bloem in een stap gezamenlijk in de papiervezelmatrix worden gebracht. Bovendien betreft de uitvinding een werkwijze waarbij plantaardige zetmeelbronnen in hun geheel, dus zonder afvalproducten te genereren, in de papierindustrie kunnen worden toegepast.

Aldus betreft de uitvinding papier of karton dat eiwit en zetmeel, althans gedeeltelijk uit dezelfde bron afkomstig, in de papiervezelmatrix omvat. Voorts betreft de uitvinding papier of karton waarin alle componenten van plantaardige zetmeel/eiwit-bronnen zijn verwerkt.

Er is gevonden dat onder toepassing van een hoeveelheid 35 bloem volgens de uitvinding papier kan worden gekregen dat in hoofdzaak dezelfde eigenschappen heeft als papier waarin ongeveer dezelfde hoeveelheid zetmeel is toegepast. Met andere woorden de functie van een deel van het conventioneel

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benodigde zetmeel kan worden overgenomen door de eiwitfractie in bloem, hoewel de stand der techniek slechts nadelige eigenschappen leert. Naast economische voordelen - bloem is goedkoper dan daaruit bereid zetmeel - worden ook technologische en milieutechnische voordelen verkregen omdat geen droogstappen of zuiveringsstappen hoeven te worden uitgevoerd en/of omdat geen afvalstromen hoeven te worden afgevoerd.

Het papier volgens de uitvinding omvat bij voorkeur ten 10 minste 0,1 gew.%, liever ten minste 0,3 gew.%, en gebruikelijk 0,3-8 gew.% zetmeel alsmede ten minste 0,03 gew.%, liever tussen 0,05 gew.% en 2,4 gew.%, gebruikelijk 0,05-1 gew.% eiwit in de papiervezelmatrix, betrokken op het gewicht van de droge stof. Indien minder dan de minimale gehalten eiwit en 15 zetmeel wordt toegepast worden de voordelen volgens de onderhavige uitvinding in een te geringe mate verkregen of zijn andere conventionele hulpstoffen vereist om de gewenste papiereigenschappen te verkrijgen. Indien meer dan 8 gew.% zetmeel en meer dan 1 gew.% eiwit worden toegepast, wordt 20 weliswaar papier met een zeer hoge toegevoegde waarde verkregen doch is het proces vanuit bedrijfseconomisch oogpunt vaak minder aantrekkelijk.

Het liefst wordt 2-5 gew.% zetmeel naast 0,2-1 gew.% eiwit in de papiervezelmatrix gebracht aangezien dit de voordelen van de uitvinding combineert met een gunstige productieprijs.

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Volgens de onderhavige uitvinding is de eiwit- en zetmeelfractie ten minste gedeeltelijk afkomstig uit een en dezelfde plantaardige bron. Als plantaardige bronnen die hiervoor kunnen worden toegepast, kunnen die worden genoemd, die een hoog gehalte aan zetmeel naast eiwit bevatten, bijvoorbeeld zaden, zoals bonen, erwten en graankorrels, bijvoorbeeld tarwe-, mais- en rijstkorrels; en andere eiwit- en hoog zetmeelhoudende plantendelen. Deze producten worden in de onderhavige beschrijving en conclusies aangeduid met de term "bloem".

Bij voorkeur wordt bloem afkomstig van granen of peulvruchten, het liefst tarwebloem, in de vezelmassa van het

papier of karton gebracht. Een groot voordeel van het toepassen van bloem afkomstig van granen en peulvruchten is dat deze grondstof voor toepassing overeenkomstig de onderhavige uitvinding vanuit een economisch oogpunt aantrekkelijker is dan toepassing van het standaard gebruikte zetmeel. Zo bedragen de kosten van tarwebloem op dit moment ongeveer de helft van die van natief tarwezetmeel.

Door het achterwege laten van de scheiding van bloem in een zetmeel- en een eiwitcomponent wordt voorts het energieverbruik aanzienlijk gereduceerd mede omdat droogstappen niet hoeven worden uitgevoerd.

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Bloem afkomstig van granen of peulvruchten, en in het bijzonder tarwebloem, wordt toegepast in hoeveelheden van bij voorkeur 2-5 gew.% betrokken op de droge massa.

Tarwebloem kan niet als zodanig in het papier worden gebracht. Indien dit wordt geprobeerd, treden de nadelen bekend uit de stand der techniek - sterke mate van afzetting, klontering, deegvorming, schuimvorming - op. Deze problemen blijken zich niet voor te doen wanneer de bloem ten minste wordt onderworpen aan een voor natief zetmeel in de papierindustrie bekende behandeling.

Voor toepassing op de lijmpers is - zoals de deskundige weet - een in water opgelost product met een Brookfield viscositeit van minder dan ongeveer 100 cP benodigd. Een dergelijke oplossing (geschikt wordt uitgegaan van een 10 gew.%-ige bloemsuspensie) kan worden verkregen door tarwebloem te behandelen met een chemisch en/of enzymatisch zetmeelketen degraderend middel tot een viscositeit in het voornoemde traject wordt bereikt. Zo kan men bijvoorbeeld bloem onderwerpen aan een voor natief zetmeel bekende degradatie met ammoniumpersulfaat (APS), eventueel in aanwezigheid van een zuur, bijvoorbeeld azijnzuur of citroenzuur. De aanwezigheid van zuur in deze uitvoeringsvorm is bijvoorbeeld benodigd indien wordt uitgegaan van tarwebloem hetgeen in voorbeeld 2 wordt geïllustreerd. Andere methoden zijn behandelingen met amylases of combinaties daarvan met APS, eventueel aangevuld met een eiwitmodificerende stap.

Waar voor een storingsvrije lijmpersbehandeling de viscositeit van uit de stand der techniek bekende natiefzetmeeloplossingen bij voorkeur tussen ongeveer 30 en 80 cP, kan worden volstaan met een viscositeit van zo laag als slechts 15 cP wanneer bloem wordt toegepast. Uit het onderstaande voorbeeld 1 blijkt dat hierbij een papier wordt verkregen van eenzelfde kwaliteit als wanneer alleen zetmeel wordt toegepast.

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Overigens is het ook mogelijk storende eigenschappen veroorzaakt doot de eiwitcomponent in bloem te elimineren door deze eiwitcomponent in hoofdzaak af te breken en aldus alleen de zetmeelcomponent effectief te benutten. Deze uitvoeringsvorm mist evenwel een aantal van de voordelen van de onderhavige uitvinding.

15 In de Nederlandse octrooiaanvrage 1001218 is beschreven dat eiwitten de sterkte-eigenschappen van papier en karton kunnen verbeteren en daarnaast een groot aantal voordelen bezitten, wanneer zij in de papiervezelmatrix aanwezig zijn. Met name geven eiwitten naast verbeterde stijfheidswaarden onder andere SCT- ("Shortspan Compression Test"), RCT- ("Ring 20 Crush Test"), en CMT- ("Concora Medium Test")waarden - en sterktewaarden - onder andere berstdruk, treksterkte -, welke waarden een maat zijn voor bepaalde sterkte-eigenschappen van het papier, vooral bij de productie van golfkarton, 25 optimalisatiemogelijkheden en verbeteringen in andere constructieve papiereigenschappen, zoals stijfheid, in verwerkbaarheidseigenschappen, zoals vouw- en rilbaarheid, en in functionele eigenschappen, zoals doorlatendheid voor gassen en vloeistoffen. Bovendien geeft de toepassing van eiwitten 30 bij de papierfabricage optimalisatiemogelijkheden en verbeteringen op het vlak van de algehele procesvoering, inzetbaarheid van grond- en hulpstoffen, en energiebehoefte. Verder kunnen voornoemde eigenschappen afhankelijk van de vervaardigingsomstandigheden en toepassingsomstandigheden, 35 bijvoorbeeld klimatologische omstandigheden, worden geregeld, zonder dat een en ander ten koste gaat van de herverwerkbaarheid van het papierproduct en het rendement van het productieproces.

Volgens de onderhavige uitvinding is nu gevonden dat de voordelen die genoemd worden in de Nederlandse octrooiaanvrage 1001218 ook kunnen worden verkregen onder toepassing van bloembestanddelen in papier. Daartoe moet niet alleen de eenstapsbehandeling als bekend voor natief zetmeel worden 5 uitgevoerd, doch moet ook een tweede bewerking worden uitgevoerd. Deze tweede bewerking is voor de toepassing van tarwebloem met de lijmpers een deamideringsreactie en/of een gedeeltelijke proteolyse. Deze tweede bewerking maakt de tarwegluten meer in water oplosbaar en kan zowel langs thermo-10 chemische (verwarmen met zuur) als langs enzymatische weg (protease) worden uitgevoerd.

In een voorkeursuitvoeringsvorm wordt de tarwebloem behandeld met zuur APS bij een temperatuur van ongeveer 85-95°C. Deze behandeling geeft naast de degradatie van het zetmeel tegelijk een bewerking van het eiwit.

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Zoals uit de onderstaande voorbeelden blijkt treden synergistische effecten op wanneer een ongescheiden bereid zetmeel/eiwitmengsel conform de uitvinding wordt toegepast. Het effect van bloem op de sterkte- en stijfheidseigenschappen 20 van papier is even groot als en soms zelfs groter dan het effect van een ongeveer even grote gewichtsfractie conventioneel behandeld en toegepast, natief zetmeel.

Aangetoond is dat door het inbrengen van eiwit- en zetmeelmoleculen in de papiervezelmassa met name de 25 stijfheids- en sterkte-eigenschappen positief kunnen worden gemodificeerd en beheersbaar kunnen worden beïnvloed.

Deze papiereigenschappen zijn niet alleen van belang bij verpakkingspapieren op basis van gerecirculeerd materiaal doch ook voor massief karton en diverse papiersoorten op basis van "virgin fibre".

Voor het verkrijgen van een goed papierproduct is het essentieel dat de eiwit- en/of zetmeelmoleculen in het papierblad aanwezig zijn. De optimalisatie van de vezel-vezelbinding van het papier, waardoor - waarschijnlijk - de 35 verkregen voordelen kunnen worden verklaard, kan immers alleen dan plaats hebben, wanneer voldoende eiwit- en/of zetmeelmateriaal op, in en tussen de vezels aanwezig is. Aldus

vormen de papiervezelmassa en de eiwit- en zetmeelfractie een geheel; er worden geen duidelijk scherp begrensde eiwit- en zetmeelmassa's en papiervezelmassa's onderscheiden.

De van voordeel zijnde effecten van het toepassen van eiwit in combinatie met zetmeel in de bulk van het papier zijn afhankelijk, soms zelfs in sterke mate, van de plaats of wijze van opbrengen en/of de aard van het ingebrachte eiwit. Na kennisnemen van de beschrijving van de onderhavige uitvinding zal het in het bereik van de deskundige liggen het papierfabricageproces, inclusief de toe te passen grond- en hulpstoffen, afhankelijk van de wensen van de afnemer/gebruiker en de omstandigheden aan te passen.

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Deze voornoemde bloembewerkingswijzen brengen in het algemeen en in hoofdzaak de eiwitfractie in oplossing, terwijl het zetmeel oplosbaar wordt gemaakt en wordt afgebroken. De bewerking van de bloem kan zowel batch-gewijs als continu-in-lijn worden uitgevoerd.

Voorts betreft de uitvinding een werkwijze voor het vervaardigen van papier of karton, omvattende ten minste een stap waarbij eiwitten en zetmeel, dat wil zeggen het product zoals het wordt gewonnen uit een natuurproduct als ongescheiden plantaardig eiwit/zetmeelmengsel, eventueel na onderwerping aan de boven uitgewerkte behandeling analoog aan die wordt uitgevoerd met natief zetmeel, in de papiervezelmatrix worden gebracht.

In conventionele papierfabricageprocessen bestaat de eerste bewerking uit het zogenaamde pulpen - het bereiden van pulp door het suspenderen van vezelmaterialen in al dan niet gerecirculeerd papier. In een grote kuip wordt onder toepassing van mechanische energie, gewoonlijk door roeren, en verwarmen, gebruikelijk met stoom of warm water, vezelmateriaal toegevoegd aan water. Door de mechanische en fysische bewerking wordt het vezelmateriaal opgelost ofwel zo gedispergeerd, dat een vloeibare pap, de pulp, ontstaat.

35 Vervolgens wordt de pulp onderworpen aan een aantal bewerkingen. Zo wordt de pulp gereinigd, waarbij de pulp wordt ontdaan van onbruikbaar, niet-vezelig materiaal. Bovendien

wordt eventueel een vezelbehandeling, zoals malen, uitgevoerd.

Tot slot wordt de pulp in een bepaalde concentratie aangeboden aan de papiermachine die uit de pulp papier vervaardigt.

Volgens de uitvinding wordt tijdens de werkwijze voor het vervaardigen van papier ten minste een stap uitgevoerd waarbij eiwitten en zetmeel gezamenlijk in de papiervezelmatrix worden gebracht.

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Tijdens de procesgang van pulpkuip naar papiermachine kunnen hulpstoffen, waaronder het volgens de onderhavige uitvinding toegepaste eiwit-zetmeelmengsel, bij voorkeur tarwebloem, worden toegevoegd. Bovendien kan het eiwit- en zetmeelmateriaal na de bladformatie daarop worden aangebracht en - door bepaalde bewerkingen uit te voeren - vervolgens in de vezelmatrix worden gebracht.

Zo kunnen tijdens de papierbladvorming eiwitzetmeeloplossingen in de papierlaag of tussen eventueel verschillende papierlagen worden gebracht, bijvoorbeeld door sproeien of schuimen. Ook kan het eiwitzetmeelmateriaal middels een oppervlaktebehandeling c.q. impregnering van het reeds gevormde papier, bijvoorbeeld en bij voorkeur door middel van een lijmpersbehandeling, in de vezelmassa worden gebracht. Tenslotte wordt op de mogelijkheid gewezen waarbij met versproeiing of andere bekende applicatietechnieken eiwitmateriaal op de droge papierbaan wordt aangebracht.

In een voorkeursuitvoeringsvorm van de werkwijze
volgens de uitvinding worden eiwit-zetmeelmengsels door middel
van een lijmpersbehandeling in het papier gebracht. Tijdens de
lijmpersbehandeling - een behandeling die algemeen in de
papierindustrie wordt toegepast en derhalve bekend is aan de
deskundige - wordt een oplossing of suspensie met daarin het
toe te passen eiwit-zetmeelmengsel door middel van walsen in
het papier geperst. De lijmpersbehandeling kan zowel
enkelzijdig aan de boven- of onderzijde van de papierbaan als
dubbelzijdig worden uitgevoerd.

Met name voor toepassing in de lijmpers hebben hogere eiwit- en zetmeelconcentraties voordelen wat betreft de maximaal haalbare eigenschappen en verminderde droogenergie die hierdoor nodig is.

Bij de voornoemde technieken is het steeds van belang dat ten minste een deel van de eiwitten en het zetmeel in innig contact met de vezels in de papiervezelmatrix wordt gebracht.

Overigens is het mogelijk naast het gezamenlijk inbrengen van een eiwit/zetmeelmengsel, nog aanvullende hoeveelheden zetmeel of eiwit in te brengen. Dit kan op dezelfde plaats onder toepassing van dezelfde techniek geschieden doch ook op andere plaatsen in het papierbereidingsproces.

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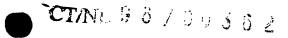
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De uitvinding betreft de toepassing van bloembestanddelen in de vezelmatrix van papier voor het verbeteren van en het richting geven aan papiereigenschappen, zoals sterkte, stijfheid, permeabiliteit, oppervlakteeigenschappen en elasticiteit. Bovendien kan de volgens de uitvinding behandelde bloemfractie worden toegepast als lijm voor het vastzetten van de golven in golfkarton.

Eveneens betreft de uitvinding het gebruik van eiwiten zetmeelhoudende materialen waarbij voor het bereiken van de gewenste papier-eigenschappen alleen de zetmeelfractie chemisch of enzymatisch wordt gemodificeerd. Indien het uitgangsmateriaal naast zetmeel bijvoorbeeld wateroplosbare eiwitten bevat, is het niet noodzakelijk om deze eiwitten te modificeren teneinde een lijm te maken met goede verwerkingsen versterkende eigenschappen. Een voorbeeld hiervan is erwtenmeel waarvan de eiwitten oplosbaar zijn in een alkalisch milieu.

Bovendien is het mogelijk om van zetmeel en eiwithoudende materialen slechts de zetmeelfractie te gebruiken om het papier te versterken. Enerzijds kan dit geschieden door het feit dat het eiwit zonder dit te modificeren dusdanig wateroplosbaar is dat het of tijdens de papierbehandeling door het papier wordt geperst of aanwezig in de papiermatrix niet bijdraagt aan de papiereigenschappen. Anderzijds kan het eiwit te ver worden gemodificeerd zodat het eveneens niet bijdraagt aan de papier-eigenschappen. In het meest extreme geval wordt het eiwit afgebroken tot aminozuren. Een voordeel hiervan is dat geen scherp begrensde



bewerkingsgraad van het eiwit hoeft te worden ingesteld waardoor het omzetten van zetmeel en eiwithoudend materiaal in het geschikte lijm een weinig kritisch proces is.

Tot slot betreft de uitvinding een werkwijze voor het 5 vervaardigen van papier, waarbij plantaardige materiaal met als hoofdcomponenten eiwit- en zetmeel, bij voorkeur graan, volledig wordt verwerkt, omvattende (i) het scheiden van het plantaardige materiaal in (a) een fractie die in hoofdzaak bestaat uit het cellulosemateriaal en (b) een fractie die in hoofdzaak bestaat uit het eiwit- en zetmeelmateriaal, het 10 toevoeren van fractie (a) aan de gebruikelijke uitgangspapier vezelmassa, bijvoorbeeld bij de pulpbereiding, en het toevoeren van de fractie (b) in de stap waarbij vezelversterkende additieven worden ingebracht. De fractie die 15 in de stap waarbij vezelversterkte additieven worden ingebracht wordt toegevoegd, wordt conform de boven beschreven werkwijze behandeld.

Met name is het bij dit aspect van de uitvinding mogelijk een plantaardige eiwit- en zetmeelbron, bijvoorbeeld 20 tarwe, volledig te vermalen en het vermalen product direct na een voor natief zetmeel analoge modificatie en eventueel na een modificatie waarbij de eiwiteigenschappen worden geoptimaliseerd - als vezelversterkende, kwaliteitsverbeterende component toe te passen, en de 25 restproducten, zoals het kaf direct als vezelmateriaal toe te passen. De modificatie van de bloem kan bestaan uit een thermochemische omzetting, bijvoorbeeld met APS en/of zuur, bijvoorbeeld citroenzuur, al dan niet in combinatie met een enzymatische modificatie met bijvoorbeelde amylase en/of 30 protease.

Thans zal de uitvinding nader worden toegelicht aan de hand van de volgende voorbeelden.

Voorbeeld 1

In dit voorbeeld werd het effect van het toepassen van bloem (IJsvogelbloem, Meneba Nederland; vochtgehalte 13,5%; ongeveer 10 gew.% gluten en ongeveer 89,5 gew.% zetmeel betrokken op het droge product) bestudeerd. Daartoe werden

suspensies van bloem en - ter vergelijking - natief zetmeel door middel van de lijmpersmethode in papier gebracht.

De oplossingen van de voornoemde macromoleculen werden op een gewenste viscositeit ingesteld door zowel de zetmeelals de bloemfractie te onderwerpen aan een degradatie met ammoniumpersulfaat (95°C). De viscositeit van de zetmeelsuspensie moet voor een storingsvrije lijmpersapplicatie tussen 30 en 80 cP liggen; goede resultaten worden bij de bloemsuspensie reeds verkregen bij een viscositeit van slechts 15 cP.

De macromoleculen-bevattende oplossingen werden met behulp van een laboratorium-lijmpers (Einlehner, snelheid 30 m/min, temperatuur 70°C, druk 2 bar) in papier (gerecycled papier; D-Liner; Roermond Papier) gebracht.

De SCT-waarde en de berstfactor werden volgens genormeerde voorschriften bepaald.

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De SCT-waarde is de maximale compressiekracht per breedte-eenheid die een teststrook onder gedefinieerde omstandigheden kan ondergaan tot deze strook stuikt. In dit voorbeeld werd de SCT-bepaling loodrecht op de looprichting van het papier uitgevoerd. De SCT-waarde wordt uitgedrukt in kN/m.

De berstfactor wordt uit een berstdrukmeting bepaald. De berstdruk is de druk die op een stuk papier wordt uitgeoefend op het moment dat het papier barst. De berstfactor (uitgedrukt in kPa) is gelijk aan de berstdruk vermenigvuldigd met 100 gedeeld door het basisgewicht (g/m^2) .

De resultaten staan in de volgende tabel vermeld.

TABEL 1 Verhoging van de SCT-waarde en de berstfactor ten opzichte van de controle bij het gebruik van bloem of zetmeel.

	SCT-waarde (kN/m)	berstfactor (kPa)
zetmeel	0,75	48
bloem	0,65	42

6 7 90382

Het is gebleken dat de toepassing van bloem nagenoeg dezelfde verhoging in SCT-waarde en berstfactor geeft als zetmeel. Bovendien kan een verdere beïnvloeding van de sterkte-eigenschappen worden verkregen door een bloemsuspensie toe te passen met een andere viscositeit.

<u>Voorbeeld 2</u>: voorbehandelingen van bloemslurries

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- A) behandeling met neutraal APS
 Een suspensie van 694 g IJsvogelbloem in 1306 g water (50°C)
 werd in een bekerglas geroerd. 2,16 g APS werd toegevoegd,
 waarna nog 30 minuten bij 50°C werd geroerd. De verkregen
 oplossing werd verdund naar een 10 gew.%'s oplossing.
 Gedurende 30 minuten werd op 75°C verhit, waarna het geheel
 nog 60 minuten in een waterbad werd gekookt.
- B) behandeling met zuur APS
 Een suspensie van 232 g IJsvogelbloem in 1309 g water werd in
 een bekerglas geroerd. Citroenzuur werd toegevoegd tot een pH
 van 4, waarna 0,72 g APS werd toegevoerd. Daarna liet men het
 mengsel 60 minuten in een waterbad koken.
- C) behandeling met APS en protease

 Een suspensie van 694 g IJsvogelbloem in 1306 g water (50°C)

 werd in een bekerglas geroerd. 1000 µl Neutrase (NovoNordisk)

 werd toegevoegd, waarna nog 30 minuten bij 50°C werd geroerd.

 De verkregen oplossing werd verdund naar een 10 gew.%'s

 oplossing. 2,16 g APS werd toegevoegd. Het geheel werd 60

 minuten in een waterbad gekookt.
 - D) behandeling met amylase en protease Een suspensie van 694 g IJsvogelbloem in 1306 g water (50°C) werd in een bekerglas geroerd. 933 μ l Ban α -amylase en 1000 μ l Neutrase (beide NovoNordisk) werden toegevoegd, waarna nog 30 minuten bij 50°C werd geroerd. De verkregen oplossing werd verdund naar een 10 gew.%'s oplossing. Gedurende 30 minuten werd de temperatuur naar 75°C verhoogd. Het geheel werd daarna nog 30 minuten in een waterbad gekookt.
- Van de vier behandelde slurries A-D werd de Brookfield viscositeit in cP bepaald. De meetresultaten zijn in de volgende tabel getoond.

TABEL 2

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_			Brookfield viscositeit (cP)
A	APS		700
В	APS	citroenzuur	40
C	APS	protease	40
D	α -amylase	protease '	25

De bloemoplossingen met viscositeiten lager dan 100 cP 10 lieten zich goed op de lijmpers verwerken.

Voorbeeld 3

Met een bloemslurrie verkregen volgens methode D in voorbeeld 2 en een 10 gew.% standaard zetmeelslurrie werden proefvellen (Testliner 3 Roermond Papier, 160 x 100 mm) behandeld op een laboratoriumlijmpers (Einlewner, snelheid 30 m/min, temperatuur 70°C, druk 2 bar). De geïmpregneerde vellen werden op een droogcylinder bij 130°C gedroogd.

Van deze proefvellen zijn onder geconditioneerde 20 omstandigheden (23°C, 50% RV) de papiereigenschappen volgens genormeerde methoden bepaald. De meetgegevens zijn in de volgende tabel vermeld.

TABEL 3: Sterkte- en stijfheidseigenschappen

5	papier- eigenschap	zetmeel (standaard)	bloem (enzymatisch)	activiteit t.o.v. 100% zetmeel
	opname (%)	3,2	3,2	
	Berstfactor (kPa)	241	273	+13%
	breeklengte (m)	6454	6915	+7%
10	rek (%)	1,93	2,13	+10%
	SCT (140 g) (kN/m)	2,46	2,76	+12%
	stiffness (kNm)	1022	1036	+1%
15	CMT 30 (140 g) N	278	284	+2%

Hierin is "opname" het gewichtspercentage bloem/zetmeel t.o.v. het droge papier.

20 <u>Voorbeeld 4</u> Toepassing van erwtenmeel.

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De eiwitten in erwtenmeel zijn wateroplosbaar. Uit erwtenmeel wordt een bloemlijm gemaakt door alleen het zetmeel te modificeren. In een aantal experimenten is het zetmeel in erwtenmeel met behulp van APS of enzymen afgebroken.

TABEL 4

behandeling	lijm viscositeit (cP)	SCT-waarde (kN/m)
APS	150	niet bepaald
APS + citroen	-	
zuur	30	4,2
BAN	80	4,2
Termamyi	60	4,4

Indien een suspensie van erwtenmeel alleen wordt behandeld met APS verkrijgt de suspensie een hoge viscositeit, waardoor de lijm moeilijk is aan te brengen op papier. Door de pH van de

suspensie te verlagen met citroenzuur wordt de APS effectiever waardoor wel een lijm wordt verkregen die aan de reologische eisen voldoet. Bij het aanbrengen van deze lijm op papier wordt de SCT-waarde verhoogd. Ook de enzyme BAN en Termamyl breken in een suspensie van erwtenmeel het zetmeel voldoende af om een viscositeit te krijgen die lager is dan 100 cP. Bij het aanbrengen op papier wordt de SCT-waarde verhoogd.

<u>Voorbeeld 5</u>: proef op productieschaal

10 In een proefreactor werd een bloemslurrie met enzymen (Neutrase) gesuspendeerd. Vervolgens werd deze slurrie thermochemisch verstijfseld met ammoniumpersulfaat over een jet-cooker (NEMO-converter). De bloemslurrie werd op de papiermachine 1 (PM1) van Roermond Papier op de lijmpers 15 verwerkt.

In het bijzonder werd een praktijkproductierun van de kwaliteit Testliner 3 (RP-Maasliner) in 140 grs uitgevoerd.

Machinecondities: standaard, d.w.z.:

- 20 - grondstofsamenstelling volgens receptuur (recycled materiaal);
 - 2-laags uitvoering;
 - in-line-behandeling op lijmpers;
 - verzwaring door lijmpersbehandeling: ca. 3%;
- snelheid PM: 625 m/min; 25

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- eindvochtgehalte papier : 7%.

Tijdens deze papierproductie werd gedurende de run de lijmpersoplossing van natief tarwemeel (thermochemische conversie met ammoniumpersulfaat (APS)) vervangen door bloem (IJsvogel; conversie: zetmeel thermochemisch met APS en eiwitdeel enzymatisch m.b.v. Neutrase).

Verwerking: goed. Resultaat vergelijkbaar met 100% zetmeel. Papiereigenschappen: de papiereigenschappen zijn

gelijk/vergelijkbaar met zetmeel. Afzettingen en schuimvorming ten gevolge van gluten werden in het systeem niet geobserveerd.

2 Tame 9 5 7 3 3 5 3 2

TABEL 5: Praktijkproef Maasliner (T.L.3), RP-PM1:

5	Papiereigenschappen		Zetmeel (standaard)	Bloem	
	Gramgewicht		gr/m²	140,1	139,9
	Eindvochtgehalte		8 '	7,1	7,0
	Opname (lijm	pers)	ક	3,2	3,1
10	Berstdruk		kPa	340	335
	Berstfactor		kPa	243	239
	Breeklengte	m.r.	m	6.610	6.640
·	Rek	m.r.	8	1,90	1,90
	R.C.T.	d.r.	kN/m	1,23	1,18
15	S.C.T.	m.r.	kN/m	4,53	4,65
	S.C.T.	d.r.	kN/m	2,30	2,49
	Stiffness	m.r.	kN/m	960	940

TABEL 6: genoemde eigenschappen

5	Papiereigenschap		Eenheid	Norm
	1.	Gramgewicht	gr/m²	ISO 536
	2.	Vochtgehalte .	ક	ISO 287
	3.	Berstdruk	kPa	ISO 2758
10	4.	Berstfactor berstdruk x 100 (=) gr/m ²	kPa	ISO 2758
	10.	S.C.T.	kN/m	DIN 54518
15	11.	R.C.T.	kN/m	DIN 53134
	12.	C.M.T30	N	ISO 7263
	13.	Porositeit (volgens Bendtsen)	ml/min	ISO 5636/3
	8.	Stijfheid	kN/m	ISO 1924/2
20	5.	Treksterkt	kN/m	ISO 1924/2
	9.	Scheursterkte	mN	ISO 1974
	14.	Ply-bond (Scott-Bond)	J/m ²	Tappi UM 403
	7.	Rek	ફ	ISO 1924/2
25	6.	Breeklengte	km	ISO 1924/2

Opmerking: de bepalingen volgens 5,6,7,8,9,10,11 en 12 kunnen worden uitgevoerd in de vezellooprichting van het papier = machinerichting (m.r.) of langlopend (L.L.), dan wel in de dwarsrichting (d.r).

Voorbeeld 6

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Voorbeeld 5 werd herhaald waarbij de bloemslurrie met citroenzuur werd gesuspendeerd. De resultaten waren vergelijkbaar met die in voorbeeld 5.

Conclusies

- 1. Papier of karton omvattende de bestanddelen van bloem in de papiervezelmatrix.
- 2. Papier of karton volgens conclusie 1, omvattende 0,1-8 gew.% zetmeel en 0,3-2,4 gew.% eiwit in de papiervezelmatrix, betrokken op het gewicht van de droge stof.
- 3. Papier of karton volgens conclusie 1 of 2, omvattende 2-5 gew.% zetmeel en 0,2-1 gew.% eiwit in de papiervezel-matrix.
- Papier of karton volgens een der voorgaande conclusies,
 waarbij de bestanddelen afkomstig zijn uit landbouwkundige producten, bijvoorbeeld peulvruchten en granen zoals erwtenmeel en tarwebloem.
 - 5. Werkwijze voor het vervaardigen van papier of karton, omvattende ten minste bloem wordt onderworpen aan een voor
- natief zetmeel in de papierindustrie bekende behandeling waarna de behandelde bestanddelen van bloem in een stap gezamenlijk in de papiervezelmatrix worden gebracht.
 - 6. Werkwijze volgens conclusie 5, waarbij de bloem wordt behandeld met een chemisch en/of enzymatisch zetmeelketen
- degraderend middel en vervolgens onder toepassing van een lijmpers in de papiervezel matrix wordt gebracht.
 - 7. Werkwijze volgens conclusie 6, waarbij de eiwitfractie van de bloem in water oplosbaar wordt gemaakt.
 8. Werkwijze waar b
- 8. Werkwijze voor het vervaardigen van papier, waarbij
 plantaardige materiaal met een hoog eiwit- en zetmeelgehalte,
 bij voorkeur graan, volledig wordt verwerkt, omvattende het
 scheiden van het plantaardige materiaal in (a) een fractie die
 in hoofdzaak bestaat uit het cellulosemateriaal en (b) een
 fractie die in hoofdzaak bestaat uit het eiwit- en
- zetmeelmateriaal, het toevoeren van fractie (a) aan de gebruikelijke vezelmassa, en het toevoeren van de fractie (b) volgens een der conclusies 5-7 in een stap waarbij vezelversterkende additieven worden ingebracht.

- 9. Toepassing van niet van elkaar gescheiden bloembestanddelen in de vezelmatrix van papier of karton voor het verbeteren of aanpassen van de sterkte-eigenschappen, stijfheidseigenschappen, permeabiliteit, oppervlakteeigenschappen en elasticiteit van het papier.
- 10. Toepassing van niet van elkaar gescheiden bloembestanddelen als lijm voor het vastzetten van de golven in golfkarton.

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UITTREKSEL

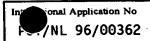
De uitvinding heeft betrekking op papier of karton dat de bestanddelen van bloem in de papiervezelmatrix omvat. Daarnaast betreft de uitvinding een werkwijze voor het vervaardigen van papier, waarbij een stap wordt uitgevoerd waarmee de bestanddelen van bloem in een gezamenlijke stap in de papiervezelmatrix wordt gebracht. Bovendien betreft de uitvinding een werkwijze waarbij een plantaardige materiaal dat een aanzienlijk hoeveelheid zetmeel en eiwit bevat volledig wordt verwerkt in een papiervervaardigingsproces. Tenslotte omvat de uitvinding de toepassing van bloembestanddelen in de vezelmatrix van papier voor het modificeren van de eigenschappen van het papier.



INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	FOR FURTHER see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.				
PCT 0501 /	ACTION	(1 0 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1			
International application No.	International filing date(dayimonthiyear)	(Earliest) Priority Date (day, month, year)		
PCT/NL 96/00362	16/09/19	96	15/09/1995		
Applicant					
ROERMOND PAPIER B.V. et a	1.		•		
This International Search Report has bee according to Article 18. A copy is being	en prepared by this Interna transmitted to the Internati	ional Searching Aut onal Bureau.	hority and is transmitted to the applicant		
This International Search Report consists Y It is also accompanied by a cop	s of a total of3	sheets. ent cited in this repor	rt		
It is also accompanied by a cop	y or cach prior are docum				
1. Certain claims were found unser	archable (see Box I).				
2. Unity of invention is lacking (se	e Box II).		·		
<u></u> .			and the second observations		
3. The international application or international search was carried	ontains disclosure of a nucl d out on the basis of the se	cotide and/or amino quence listing	acid sequence listing and the		
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·	but not accompanied matter going beyond	by a statement to the disclosure in the	he effect that it did not include : international application as filed.		
Tra	anscribed by this Authority				
4. With regard to the title, X the	e text is approved as submi	tted by the applicant			
	e text has been established				
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5. With regard to the abstract,					
نما ا	e text is approved as subm	-	t. 8.2(b), by this Authority as it appears in		
	ox III. The applicant may,	within one month fr	om the date of mailing of this International		
Se	earch Report, submit comn	ena to dia Addioi	·y.		
6. The figure of the drawings to be pu			Y None of the figures.		
	suggested by the applicant		Aone of the lightes.		
	ecause the applicant failed t ecause this figure better ch		uon.		
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D21H17/02 D21H17/22 D21H17/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 011 741 A (HOFFMAN ROGER P) 30 April	1,4-6
A	1991 see the whole document	9,10
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X	BE 331 525 A (ANTOINE) 29 January 1926 see the whole document	1,2
	-/	

Further documents are listed in the continuation of box C.	X Patent family memoers are listed in alliana.
* Special categories of cited documents: A* document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"O" document referring to an oral disclosure, use, exhibition or other means	ments, such combination being obvious to a person skilled
P document published prior to the international filing date but later than the priority date claimed	in the art. *&* document member of the same patent family
Date of the actual completion of the international search	Date of mailing of the international search report
9 January 1997	1 1. 02. 97
Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentiaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Songy, 0

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International Application No
PUNL 96/00362

	on) DOCUMENTS CONSIDERED TO BE RELEVANT	Relevant to claim No.
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BE-A-331525		NONE		
DE-A-659997		NONE		

INTERNATIONAL PRELIMINARY EX	Kopie in/naar	TERMUN		PCT
SMULDERS, Th.A.H.J. VEREENIGDE OCTROOIBUREA Nieuwe Parklaan 97 2587 BN Den Haag PAYS-BAS	24 30		aan THE IN	CATION OF TRANSMITTAL OF TERNATIONAL PRELIMINARY EXAMINATION REPORT (PCT Rule 71.1)
nat lane 15-3-98			Date of mailing (day/month/year)	1 9. 12. 97
Applicant's or agent's file reference PCT 0501				IMPORTANT NOTIFICATION
International application No. International filing date (d PCT/NL96/00362 16/09/1996			day/month/year)	Priority date (day/month/year) 15/09/1995
Applicant				

- 1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
- 2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
- 3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

9))

European Patent Office D-80298 Munich

Tel (+49-89) 2399-0. Tx: 523656 epmu d

Fax. (+49-89) 2399-4465

Authorized officer

Hanrieder-Kreuzer, K

Tel (+49-89) 2399-8132



PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

or applicant's or	agents	s file reference	FOR FURTHER ACTION	See Preli	Notification of Transmittal of International iminary Examination Report (PCT/IPEA/416)
PCT 0501			1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		Priority date (day/month/year)
nternational a			International filing date (day/month/year	7	
PCT/NL96/			16/09/1996		15/09/1995
nternational P	atent (Classification (IPC) or na	ational classification and IPC		
21H17/02	2				
pplicant					
ROERMON	ID PA	APIER B.V. et al.			
and is to	ransm	itted to the applicant	according to Article 36.		ternational Preliminary Examining Authority
2. This RE	POR	T consists of a total o	of 6 sheets, including this cover she	et.	
· · · · · · · · · · · · · · · · · · ·		es consist of a total c	of sheets.		
	_				
11	Ø	Basis of the report			
11		Priority Non-establishment	of opinion with regard to novelty, inv	entive :	step and industrial applicability
III 177		Lack of unity of inve	•		
IV V	∐ ⊠	Reasoned stateme	nt under Article 35(2) with regard to re nations supporting such statement	novelty	, inventive step or industrial applicability;
VI ·	. 🗀	Certain documents			
VII	×		he international application		
VIII	_ ⊠	Certain observation	ns on the international application		
Date of sub	missio	n of the demand	Date of co	ompletio	n of this report
08/04/19					5 9 2 5



European Patent Office D-80298 Munich

Name and mailing address of the IPEA/

Tel. (+49-89) 2399-0. Tx 523656 epmu d

Fax (+49-89) 2399-4465

Karlsson. B

Authorized officer

Telephone No (+49-89) 2399-8424



INTERNATIONAL PRELIMINARY **EXAMINATION REPORT**

International application No. PCT/NL96/00362

l.	Basis	of the	report
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	Basis of the report			
1.	This report has beer response to an invita the report since they	ation under Articl	le 14 are i	substitute sheets which have been furnished to the receiving Office in referred to in this report as "originally filed" and are not annexed to ents.):
	Description, pages	•		
	1-19	as originally f	iled	
	Claims, No.:			
	1-10	as originally	filed	
2.	The amendments ha	ave resulted in th	ne cancell	lation of:
	☐ the description,	pages:		
	☐ the claims,	Nos		
	☐ the drawings,	sheets:		
3.	☐ This report has considered to g	been establishe go beyond the di	d as if (so sclosure a	ome of) the amendments had not been made, since they have been as filed (Rule 70.2(c)):
4.	Additional observat	ions, if necessar	y:	
V	. Reasoned stateme applicability; citat	ent under Articl ions and explar	ė 35(2) w nations si	vith regard to novelty, inventive step or industrial supporting such statement
1	Statement	•		
	Novelty (N)	Yes: No:	Claims Claims	3,4,6-8,10 1,2,5,9
	Inventive step (IS)	Yes: No:	Claims Claims	

Claims 1-10

Claims

Yes:

No:

Industrial applicability (IA)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL96/00362

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

course, a protein separation operation not necessary. A more simplified process is then gained. However, firstly, such a process has not been clearly defined in the present claim 5 and, secondly, according to the description it appears as some other additional process operation instead would be necessary (see Page 8, first paragraph). Thus, a clarified process claim may fulfill the requirements of Articles 33.2 and 33.3 PCT.

- 1.7 To use flour components, i.e. a starch/protein mixture appears to be known from D1 and D2. The subject-matter of the present claim 9 is thus known from D1 or D2 (see remarks above). No inventive matter can be traced in the features of claim 10 in the light of the diclosures of D1 and D2.
- 2. D1 and D2 should be acknowledged in the description as representing closest prior art (Rule 5.1(a)(i)-(vi) PCT.
- 3.1 The wording "comprising the components of flour in the paper fiber matrix" in claim 1 has not been clearly defined (Art.6 PCT). The word "flour" refers to the grounded wheat grains, wherein the separated endosperms consists of about 70-80% of starch and 10-15% of protein, i.e. the state of the starch/protein mixture when it is being added to the fibre matrix in the beginning of the paper manufacturing process. Therefore, the rather misleading word "flour" should be clarified by defining the starch/protein mixture, and its respective percentage values, in the paper as defined in claim 1 (cf. claim 2).

 The corresponding remarks also apply to claim 9.
- 3.2 The wording "flour is subjected to a treatment known in the paper industry for native starch" causes unclarity. The mentioned wording should be deleted and instead replaced with the necessary process steps. From the whole specification it becomes clear that the present invention is based on the discovery that the starch/protein mixture from the grounded grains can be used, as such, without firstly separating the protein from the starch, while the same properties of the produced paper results. Accordingly, the necessary process-steps, i.e. the essential features of claim 8 should thus be introduced into claim 5 (Art.6 PCT; see further comments under section V). It should further also explicitly be defined

INTERNATIONAL PRELIMINARY

International application No. PCT/NL96/00362

EXAMINATION REPORT - SEPARATE SHEET

in claim 5 that the starch/protein mixture results from the same source.

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	or agent's file reference FOR FURTHER see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below				
PCT 0501	ACTION	220) as well as, where applicable, term 5 of our			
International application No.	International filing date(day/month/year)	(Earliest) Priority Date (day/month/year)			
PCT/NL 96/00362	16/09/1996	15/09/1995			
Applicant					
ROERMOND PAPIER B.V. et a	1.				
This International Search Report has bee according to Article 18. A copy is being	en prepared by this International Searching Autransmitted to the International Bureau.	thority and is transmitted to the applicant			
This International Search Report consist. X It is also accompanied by a cop	s of a total of sheets. by of each prior art document cited in this repo	ort.			
Certain claims were found unsea	archable (see Box I).				
2. Unity of invention is lacking (se	e Box II).	·			
	ontains disclosure of a nucleotide and/or amino	acid sequence listing and the			
file	d with the international application.				
fur	nished by the applicant separately from the int	ernational application,			
	but not accompanied by a statement to the matter going beyond the disclosure in the				
Tra	anscribed by this Authority				
, (2)	text is approved as submitted by the applicant				
the	text has been established by this Authority to	read as follows:			
		·			
5. With regard to the abstract,	the state of the s				
	e text is approved as submitted by the applican te text has been established, according to Rule 3				
	ox III. The applicant may, within one month fr arch Report, submit comments to this Authori	om the date of mailing of this International			
6. The figure of the drawings to be pul	blished with the abstract is:				
Figure No as	suggested by the applicant.	X None of the figures.			
be	cause the applicant failed to suggest a figure.	•			
be	cause this figure better characterizes the invent	ion.			



A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D21H17/02 D21H17/22 D21H17/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) IPC 6 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

0.000.	MENTS CONSIDERED TO BE RELEVANT	D. 1
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Х	US 5 011 741 A (HOFFMAN ROGER P) 30 April	1,4-6
Α	see the whole document	9,10
X	EP 0 546 956 A (GOMEZ DANIEL ;TECH DU PAPIER CENTRE (FR)) 16 June 1993 see claims 2,3	1,4,5,9
X	US 3 166 466 A (PUYDAK) 19 January 1965 see claim 1	1-3
Х	US 1 755 744 A (MUNKTELL) 22 April 1930 see the whole document	1,2
X	BE 331 525 A (ANTOINE) 29 January 1926 see the whole document	1,2
	-/	

X Further documents are listed in the continuation of box C.	Patent family members are listed in annex.
 Special categories of cited documents: 'A' document defining the general state of the art which is not considered to be of particular relevance 'E' earlier document but published on or after the international filing date 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) 'O' document referring to an oral disclosure, use, exhibition or other means 'P' document published prior to the international filing date but later than the priority date claimed 	 "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family
Date of the actual completion of the international search	Date of mailing of the international search report
9 January 1997	1 1. 02. 97
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2	Authorized officer
NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Songy, 0

Form PCT/ISA/210 (second sheet) (July 1992)

1



International Application No
PC L 96/00362

(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT	10.000
Category Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
DE 659 997 A (WENZEL) 13 May 1938 see the whole document	1,2
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1

Information on patent family members

Into mal Application No
PCT/NL 96/00362

Patent document cited in search report	Publication date		t family iber(s)	Publication date
US-A-5011741	30-04-91	AU-B- AU-A- CA-A- DE-D- DE-T- EP-A- JP-A-	629739 7351891 2038638 69104249 69104249 0448344 4214497	08-10-92 26-09-91 21-09-91 03-11-94 16-03-95 25-09-91 05-08-92
 EP-A-0546956	16-06-93	FR-A-	2684966	18-06-93
US-A-3166466	19-01-65	NONE		
US-A-1755744	22-04-30	NONE		
BE-A-331525		NONE		
DE-A-659997		NONE		



PATENT COOPERATION TREATY

PCT

C'D	2	4	DEC	1997
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or PCT 0501	agenť	s file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (PCT/IPEA/416)
nternational a		tion No	International filing date (day/month/year	Priority date (day/month/year)
PCT/NL96	• •		16/09/1996	15/09/1995
			ational classification and IPC	
)21H17/02		Classification (ii G) of the		
2211117702	-			
Applicant				
ROERMON	ND P	APIER B.V. et al.		
1. This int	ernati	onal preliminary exam	nination report has been prepared by	this International Preliminary Examining Authority
and is t	ransm	itted to the applicant	according to Article 36.	·
2. This RE	:POR	T consists of a total of	f 6 sheets, including this cover shee	∍t .
☐ Th	is rep	ort is also accompani	ed by ANNEXES, i.e., sheets of the	description, claims and/or drawings
wh	nich ha	eve been amended ar	nd are the basis for this report and/or	r sheets containing rectifications made
be	tore tr	nis Authority (see Hui	3 70.16 and Section 607 of the Admi	nistrative Instructions under the PCT).
These :	anney	es consist of a total o	f sheets.	
111000	2111102	00 00110101 01 0 10101 0		
3. This rep	port co	ontains indications rel	ating to the following items:	
1	⊠	Basis of the report		
II		Priority		
Ш		Non-establishment	of opinion with regard to novelty, inve	entive step and industrial applicability
IV		Lack of unity of inve	ntion	
V	\boxtimes	Reasoned statemen	nt under Article 35(2) with regard to n ations supporting such statement	ovelty, inventive step or industrial applicability;
VI	П	Certain documents		
VII	⋈		e international application	
VIII	⊠ R21		s on the international application	
VIII	Δ	Certain observations	5 Of the international application	
Data of sub-		of the demand	Date of cou	mpletion of this report
Date of subr	nission	or the demand	Date of con	
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00/0 // 100				
		address of the IPEA/	Authorized	officer
Name and n	nailing			The state of the s
Name and n				(s =
Name and n	Euro D-80	opean Patent Office 0298 Munich (+49-89) 2399-0, Tx: 52	Karlsson	о, В

Fax: (+49-89) 2399-4465

INTERNATIONAL PRELIMINARY **EXAMINATION REPORT**

International application No. PCT/NL96/00362

in

I.	Bas	is	of '	the	report
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١.	Das	as of the report			
1.	resp	s report has been d conse to an invitation report since they d	on under Artic	le 14 are	substitute sheets which have been furnished to the receiving Office referred to in this report as "originally filed" and are not annexed to ents.):
	Des	cription, pages:			
	1-19	e	as originally t	iled	
	Cla	ims, No.:			
	1-10	0	as originally	filed	
2.	The	amendments have	e resulted in th	ne cancel	llation of:
		the description,	pages:		
		the claims,	Nos.:		
		the drawings,	sheets:		
3.		This report has be considered to go	een establishe beyond the dis	d as if (se sclosure a	come of) the amendments had not been made, since they have been as filed (Rule 70.2(c)):
4.	Add	ditional observation	s, if necessar	y :	
۷.	Rea	asoned statement blicability; citation	under Article s and explan	e 35(2) w ations s	with regard to novelty, inventive step or industrial supporting such statement
1.	Sta	tement			
	Nov	velty (N)	Yes: No:	Claims Claims	
	inv	entive step (IS)	Yes: No:	Claims Claims	
	Ind	ustrial applicability	(IA) Voc.	Claims	1-10

Claims

No:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL96/00362

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

INTERNATIONAL PRELIMINARY InterEXAMINATION REPORT - SEPARATE SHEET

- 1.1 The amended claim 1 refers to a paper which contains a mixture of starch and protein. A paper comprising the above mentioned features is already known from D1:EP-A-0 546 956 (see D1, claims 1,11,17; Examples 16, 18, Table 2). Accordingly, the subject-matter of the amended claim 1 does not meet the requirements of Art. 33.2 PCT (see further comments and references under 1.3 and 1.4 below).
- 1.2 D2:US-A-3 166 466 discloses a wood fibre product, e.g. a cardboard product, which also comprises the above mentioned features. The subject-matter of the amended claim 1 is neither novel in the light of the disclosure of D2 (Art.33.2 PCT).
- 1.3 D3:US-A-5 011 741 discloses a process for producing a cardboard product, wherein corn starch is used as the dry strength agent (see D3, column 2, last paragraph; column 5, lines 25-55). A person skilled in the art who is trying to improve the strength properties of the cardboard product, i.e. starting out from D3, would from D1 get the teaching, that the strength properties of the paper are improved when the protein, which orginates from the corn starch, is added together with the starch. Thus, the subject-matter of the amended claim 1 does not appear to be inventive in the light of the disclosure of D3 and D1 (Art.33.3 PCT).
- 1.4 No inventive matter can be seen in the additional features of claims 3 and 4 in the light of the disclosures of D1 and D2 (Art.33.3 PCT).
- 1.5 The process features of the present claim5, although presently very unclearly drafted, are known from D1 and D2 (see D1 claim 1, Examples, Table 2; see D2, figure). The present claim 5 is thus not novel with regard to the disclosures of D1 or D2 (Art.33.2 PCT).
- 1.6 It appears as if the present invention lies in the discovery that the grounded grain, i.e. a mixture of starch and protein, can be used as a paper additive obtaing the same paper quality regarding strength properties, etc. compared to a paper having only starch as additive. In such a paper manufacturing process is, of

course, a protein separation operation not necessary. A more simplified process is then gained. However, firstly, such a process has not been clearly defined in the present claim 5 and, secondly, according to the description it appears as some other additional process operation instead would be necessary (see Page 8, first paragraph). Thus, a clarified process claim may fulfill the requirements of Articles 33.2 and 33.3 PCT.

- 1.7 To use flour components, i.e. a starch/protein mixture appears to be known from D1 and D2. The subject-matter of the present claim 9 is thus known from D1 or D2 (see remarks above). No inventive matter can be traced in the features of claim 10 in the light of the diclosures of D1 and D2.
- 2. D1 and D2 should be acknowledged in the description as representing closest prior art (Rule 5.1(a)(i)-(vi) PCT.
- 3.1 The wording "comprising the components of flour in the paper fiber matrix" in claim 1 has not been clearly defined (Art.6 PCT). The word "flour" refers to the grounded wheat grains, wherein the separated endosperms consists of about 70-80% of starch and 10-15% of protein, i.e. the state of the starch/protein mixture when it is being added to the fibre matrix in the beginning of the paper manufacturing process. Therefore, the rather misleading word "flour" should be clarified by defining the starch/protein mixture, and its respective percentage values, in the paper as defined in claim 1 (cf. claim 2).

 The corresponding remarks also apply to claim 9.
- 3.2 The wording "flour is subjected to a treatment known in the paper industry for native starch" causes unclarity. The mentioned wording should be deleted and instead replaced with the necessary process steps. From the whole specification it becomes clear that the present invention is based on the discovery that the starch/protein mixture from the grounded grains can be used, as such, without firstly separating the protein from the starch, while the same properties of the produced paper results. Accordingly, the necessary process-steps, i.e. the essential features of claim 8 should thus be introduced into claim 5 (Art.6 PCT; see further comments under section V). It should further also explicitly be defined

INTERNATIONAL PRELIMINARY

International application No. PCT/NL96/00362

EXAMINATION REPORT - SEPARATE SHEET

in claim 5 that the starch/protein mixture results from the same source.

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 D21H17/02 D21H17/22

D21H17/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

 $\begin{tabular}{ll} Minimum documentation searched (classification system followed by classification symbols) \\ IPC 6 D21H \end{tabular}$

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCU	DOCUMENTS CONSIDERED TO BE RELEVANT			
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
Х	US 5 011 741 A (HOFFMAN ROGER P) 30 April	1,4-6		
Α	see the whole document	9,10		
X	EP 0 546 956 A (GOMEZ DANIEL ;TECH DU PAPIER CENTRE (FR)) 16 June 1993 see claims 2,3	1,4,5,9		
X	US 3 166 466 A (PUYDAK) 19 January 1965 see claim 1	1-3		
X	US 1 755 744 A (MUNKTELL) 22 April 1930 see the whole document	1,2		
X	BE 331 525 A (ANTOINE) 29 January 1926 see the whole document	1,2		
	-/			

X Further documents are listed in the continuation of box C.	Patent family members are listed in annex.
* Special categories of cited documents: 'A' document defining the general state of the art which is not considered to be of particular relevance 'E' earlier document but published on or after the international filing date 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) 'O' document referring to an oral disclosure, use, exhibition or other means 'P' document published prior to the international filing date but later than the priority date claimed	 "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family
Date of the actual completion of the international search 9 January 1997	Date of mailing of the international search report 1 1. 02. 97
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Authorized officer Songy, 0

	ion) DOCUMENTS CONSIDERED TO BE RELEVANT	12:
tegory °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	DE 659 997 A (WENZEL) 13 May 1938 see the whole document	1,2
	•	

information on patent family members

Inte al Application No PCT/NL 96/00362

Patent document cited in search report	Publication date		t family iber(s)	Publication date
US-A-5011741	30-04-91	AU-B- AU-A- CA-A- DE-D- DE-T- EP-A- JP-A-	629739 7351891 2038638 69104249 69104249 0448344 4214497	08-10-92 26-09-91 21-09-91 03-11-94 16-03-95 25-09-91 05-08-92
EP-A-0546956	16-06-93	FR-A-	2684966	18-06-93
US-A-3166466	19-01-65	NONE		
US-A-1755744	22-04-30	NONE		
BE-A-331525		NONE		
DE-A-659997		NONE		

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



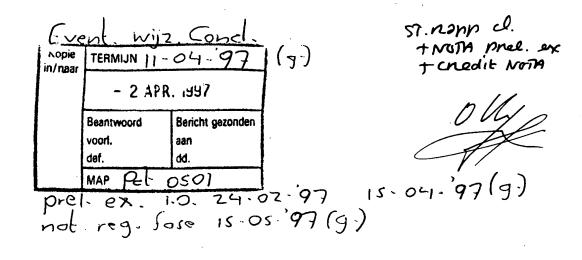
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ :		(11) International Publication Number: WO 97/10385
D21H 17/02, 17/22, 17/28	A1	(43) International Publication Date: 20 March 1997 (20.03.97)
(21) International Application Number: PCT/NLS (22) International Filing Date: 16 September 1996 (16) (30) Priority Data: 15 September 1995 (15.09.9) (71) Applicant (for all designated States except US): ROE PAPIER B.V. [NL/NL]; Mijnheerkensweg 18, NL-Roermond (NL).	16.09.9 5) N	LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).
(72) Inventors; and (75) Inventors/Applicants (for US only): VAN KESSEI Peter, Marie [NL/NL]; Ursulahof 58, NL-59 Kessel (NL). KUYPERS, Gerardus, Henricus, [NL/NL]; Cornelishoflaan 3, NL-6042 ND R (NL). MAESSEN, Matheus, Petrus, Marie [NL/N-Hövellstraat 35, NL-5988 AG Helden (NL).	995 C Andre .oermo	With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments. In English translation (filed in Dutch).
(74) Agents: SMULDERS, Th, A., H., J. et al.; Ve Octrooibureaux, Nieuwe Parklaan 97, NL-2587 Hague (NL).	ereenig BN T	de he

(54) Title: PAPER AND CARDBOARD COMPRISING STARCH- AND PROTEIN-CONTAINING MATERIAL

(57) Abstract

The invention relates to paper or cardboard comprising the components of flour in the paper fiber matrix. In addition, the invention relates to a method for manufacturing paper, wherein a step is carried out whereby the components of flour are introduced into the paper fiber matrix in a joint step. Moreover, the invention relates to a method wherein a vegetable material containing a considerable amount of starch and protein is completely processed in a paper-manufacturing process. Finally, the invention comprises the use of flour components in the fiber matrix of paper for modifying the properties of the paper.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
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BF	Burkina Faso	IE	Ireland	NZ	New Zealand
		it	Tolay	· PL	Poland
BG	Bulgaria	JP ·	Japan	PT	Portugal
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BR	Brazil	KG	Kyrgystan	· RU	Russian Federation
BY	Belarus	KP	Democratic People's Republic	SD	Sudan
CA	Canada	K	•	SE	Sweden
CF	Central African Republic		of Korea	SG	Singapore
CG	Congo	KR	Republic of Korea	SI	Slovenia
CH	Switzerland	KZ	Kazakhstan		0.0
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	; Sri Lanka	SN	Senegal
CN	China	LR	Liberia	SZ	Swaziland
CS	Czechoslovakia	LT	Lithuania	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	LV	Latvia	TJ	Tajikistan
DK	Denmark	MC	Monaco	TT .	Trinidad and Tobago
EE	Estonia	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML	Mali	US	United States of America
FR	France	MN	Mongolia	UZ.	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

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Title: Paper and cardboard comprising starch- and proteincontaining material

The invention resides in the field of paper and cardboard manufacturing. In particular, the invention relates to the use of a combination of starch- and protein-containing material in paper and cardboard. In fact, in this specification and the claims, the term 'paper' is meant to include cardboard as well.

Traditionally, starches are used on a large scale and in large volumes in the paper and cardboard industry. In the production of coated paper, which is substantially used as graphic paper in the fine-paper industry, it is used as, interalia, binding agent in the coating. In general, this starch is a modified starch.

In addition, starch is used as admixture for improving the strength properties, and in particular the dry-strength properties, of the paper. For that purpose, starches conventionally used in the paper industry and anionic and cationic derivatives of these starches are used, for which reference can be made to, for instance, EP-A-0 545 228 and WO-A-94/05855.

In this connection, further reference can be made to Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition (1981), John Wiley & Sons, Volume 16, p. 803 ff, in particular pp. 814-819.

In the most current uses of starch as fiber-reinforcing component, it is either introduced - usually in the form of cationic starch - into the mass of the paper in the wet portion of the paper process, or impregnated - substantially in the form of solubilized native starch - into the paper fiber mass by means of the so-called size press.

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These known strength-improving additives are advantageous, both in an economical and in a technical or technological sense; they give the paper or the cardboard an added value. Apart from providing an added value in conventional paper and cardboard processes, the need for additives for increasing the strength is enhanced in particular by the increasing use of weaker fibers, old paper that is reused more and more often, and a further increasing use of fillers instead of fibers in this old paper, resulting in a decreasing strength potential, and the decreasing availability of strong, long-fiber components in the base pulp for paper.

Actually, it is now emphasized that the invention is not limited to "waste-based" paper. The invention extends across the entire area of paper and cardboard manufacture, including paper based on "virgin fiber".

The known starch-based additives can enter into large-scale interactions with the cellulose groups of paper fibers. Thus, an increase of the number of bonds between the mutual paper fibers is formed, which reinforces the fiber-fiber bond and, accordingly, improves the strengh properties of the final product.

In conventional processes wherein starches are used as strengthener, strict requirements are imposed on the protein content that may be present in the starch product used. In particular, native starch used for the manufacture of paper, substantially native wheat-, corn- or potato starch, is supplied with an additional specification for maximum protein contents of 0.3-0.5 wt.%, calculated on the dry substance. Higher protein contents are supposed to have a contaminating effect and to cause lump formation and depositions in the system. For instance, the dispersion of gluten (the protein fraction in wheat flour) leads to lumping and foam formation. These drawbacks occur to an enlarged extent when these proteins are exposed to higher temperatures in the paper manufacturing process.

The starch which forms the basic material for presently used starch additives in paper is recovered from a large number of vegetable sources, for instance from grains, such as wheat, corn and rice; from tubers, such as potatoes and tapioca; or from other plant parts, such as sago.

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From the above-mentioned vegetable sources, the starch is released by the use of a combination of mechanical steps, purifying steps and drying steps. The separated protein-containing fractions, as well as other by-product fractions, are discharged. The starch purification involves the release of many waste flows, such as water flows containing biological material. These flows are increasingly becoming an environmental problem, so that draining without more is no longer possible.

The preparation of the starch that is used in the paper industry in the largest amounts as fiber-reinforcing and paper-stiffening agent, viz. wheat starch, is described as example. Similar processes are carried out for rendering starch from other vegetable sources applicable to the paper industry.

Wheat grains substantially consist of two components. The core, the so-called endosperm, largely consists of starch and protein. The outer layer, the brans or the chaff, mainly contains cellulose. The ratio core:outer layer is about 80:20.

These wheat grains are ground, the chaff being separated from the core. The separated endosperm, consisting for about 70-80% of starch and for about 10-15% of protein, is commonly designated by the term "flour". Depending on the extraction degree of the wheat, more or less pure flour is obtained. For instance, at an extraction degree of about 80%, "grey flour" is obtained, while at a somewhat lower extraction degree of about 70%, considerably purer flour is obtained, because at this extraction degree, no parts other than the endosperm end up in the flour.

In the production of starch for the paper industry, the protein, in particular the gluten, is subsequently washed from the flour. The flour is thus separated into two main

components. As indicated, in this process, economically unprofitable drying steps are carried out, a part of the starting substance wheat cannot be used, and waste flows are created that have to be processed.

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The primary object of the present invention is to provide a method wherein an optimized use is made of raw materials in the sense that a largest possible fraction of the raw material can be used in the paper process.

This object is realized by introducing the components of flour into the manufacturing process of paper or cardboard completely, without this flour or flour components being priorly modified by binding cationic or anionic groups thereto or without such protein/starch mixtures being priorly drymodified. In other words, the object is realized by starting from native protein/starch mixtures and using them as such. In this specification and claims, by "flour" is meant a protein-and starch-containing fraction originating from one and the same vegetable source, or a natural mixture of protein and starch.

More in particular, the invention relates to paper or cardboard comprising the components of native flour in the paper fiber matrix. In addition, the invention relates to a method for manufacturing paper or cardboard wherein flour is substantially subjected to a treatment whereby starch and protein are solubilized, after which the treated components of flour are jointly introduced into the paper fiber matrix in one step. Moreover, the invention relates to a method wherein vegetable starch sources can be used entirely, hence without generating waste products, in the paper industry.

Accordingly, the invention relates to paper of cardboard comprising protein and starch, at least partly originating from the same source, in the paper fiber matrix. Further, the invention relates to paper or cardboard into which all components from vegetable starch/protein sources have been processed.

It has been found that by the use of an amount of flour according to the invention, paper can be obtained which has

substantially the same properties as paper wherein about the same amount of starch is used. In other words, the function of a part of the conventionally required starch can be taken over by the protein fraction in flour, although the prior art merely teaches disadvantageous properties. In addition to economical advantages - flour is cheaper than starch prepared therefrom -, technological and environmental advantages are obtained as well, because no drying steps or purifying steps have to be carried out, and/or because no waste flows have to be discharged.

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The paper according to the invention preferably comprises at least 0.1 wt.%, more preferably at least 0.3 wt.%, and usually 0.3-8 wt.% starch and at least 0.03 wt.%, preferably between 0.05 wt.% and 2.4 wt.%, usually 0.05-1 wt.% protein in the paper fiber matrix, calculcated on the weight of the dry substance. If less than the minimum contents of protein and starch are used, the advantages obtained according to the present invention are too slight or other conventional auxiliary substances are required for obtaining the desired paper properties. It is true that if more than 8 wt.% starch and more than 1 wt.% protein is used, paper of a very high added value is obtained, but from a business-economical viewpoint, the process is often less attractive.

Preferably, 2-5 wt.% starch in addition to 0.2-1 wt.% protein is introduced into the paper fiber matrix, because this combines the advantages of the invention with a favorable production price.

In accordance with the present invention, the protein and starch fraction at least partly originates from one and the same vegetable source. As vegetable sources that can be used for this purpose, those having a high content of starch next to protein can be mentioned, for instance seeds, such as beans, peas and grains, for instance wheat, corn and rice grains; and other protein— and high starch—containing plant parts. In the present specification and claims, these products are designated by the term "flour".

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Preferably, flour originating from grains or pulses, preferably wheat flour, is introduced into the fiber mass of the paper or cardboard. A great advantage of the use of flour originating from grains and pulses is that from an economical viewpoint, for use in accordance with the present invention, this raw material is more attractive than the starch that is normally used. For instance, at this moment, the cost of wheat flour are about half the cost of native wheat starch.

Further, because of the omission of the separation of flour into a starch and protein component, the energy consumption is reduced considerably, partly because no drying steps have to be carried out.

Flour originating from grains or pulses, and in particular wheat flour, is used in amounts of preferably 2-5% calculated on the dry mass.

wheat flour cannot be introduced into the paper as such. If this is attempted, the drawbacks known from the prior art - high degree of deposition, lumping, dough formation, foam formation - occur. The problems prove not to occur when the flour is at least subjected to a treatment known for native starch in the paper industry.

As a skilled person knows, for use on the size press, a product dissolved in water and having a Brookfield viscosity of less than about 100 cP is required. Such a solution (it is suitable to start from a 10 wt.% flour suspension) can be obtained by treating wheat flour with a chemical and/or enzymatic starch chain-degrading agent to obtain a viscosity in the above-mentioned range. For instance, flour can be subjected to a degradation with ammonium persulfate (APS), known for native starch, optionally in the presence of an acid, for instance acetic acid or citric acid. The presence of acid in this embodiment is for instance needed if wheat flour is started from, which is illustrated in Example 2. Other methods are treatments with amylases or combinations thereof with APS, optionally complemented with a protein-modifying step.

Whereas for an interference-free size press treatment, the viscosity of native starch solutions known from the prior art is preferably between about 30 and 80 cP, a viscosity as low as only 15 cP is sufficient when flour is used. From Example 1 below, it appears that this produces a paper of the same quality as in the case where only starch is used.

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In fact, it is also possible to eliminate interfering properties caused by the protein component in flour by substantially degrading this protein component and, accordingly, only utilizing the starch component effectively. However, this embodiment lacks a number of the advantages of the present invention.

Dutch patent application 1001218 describes that proteins can improve the strength properties of paper and cardboard and, in addition, have a large number of advantages when they are present in the paper fiber matrix. In particular, proteins inter alia provide, apart from improved stiffness values, SCT- ("Shortspan Compression Test"), RCT-("Ring Crush Test"), and CMT- ("Concora Medium Test") values and strength values - inter alia burst pressure, tensile strength -, which values are a measure for specific strength properties of the paper, in particular for the production of corrugated board, optimization possibilities and improvements in other constructional paper properties, such as stiffness, in properties of processability, such as foldability and scoring facility, and in functional properties, such as permeability to gases and liquids. Moreover, the use of proteins in paper manufacturing provides optimization possibilities and improvements in the field of general process control, usability of raw and auxiliary materials, and energy 30 demand. Further, the above-mentioned properties can be controlled depending on the manufacturing conditions and conditions of application, for instance climatological conditions, without this being at the expense of the reprocessability of the paper product and the output of the 35 production process.

In accordance with the present invention, it has now been found that the advantages mentioned in Dutch patent application 1001218 can also be obtained by the use of flour components in paper. For that purpose, not only the one-step treatment as known for native starch should be carried out, but a second treatment should be carried out as well. For the use of wheat flour with the size press, this second treatment is a deamidation reaction and/or a partial proteolysis. This second treatment renders the wheat gluten more water-soluble and can be carried out in a thermo-chemical manner (warming by acid) as well as in an enzymatic manner (protease).

In a preferred embodiment, the wheat flour is treated with acid APS at a temperature of about 85-95°C. In addition to the degradation of the starch, this treatment provides at the same time a processing of the protein.

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As appears from the examples given below, synergistic effects occur when a starch/protein mixture prepared in an unseparated manner is used in conformity with the invention. The effect of flour on the strength and stiffness properties of paper is as great as and sometimes even greater than the effect of an approximately equally large weight fraction of conventionally treated and used, native starch.

It has been demonstrated that by introducing protein and starch molecules into the paper fiber matrix, in particular the stiffness and strength properties can be positively modified and controllably influenced.

These paper properties are not only important in respect of wrapping papers based on recirculated material, but also in respect of solid cardboard and various types of paper based on "virgin fiber".

For obtaining a good paper product, it is essential that the protein and/or starch molecules be present in the paper sheet. After all, the optimization of the fiber-fiber bond of the paper, whereby the resulting advantages can - probably - be explained, can only take place when sufficient protein and/or starch material is present on, in and between the fibers. In this manner, the paper fiber mass and the

protein and starch fraction form a whole; no clearly sharply delimited protein and starch masses and paper fiber masses are distinguished.

The advantageous effects of the use of protein in combination with starch in the bulk of the paper are dependent, sometimes even to a high degree, on the place or manner of applying and/or the nature of the protein introduced. After taking cognizance of the specification of the present invention, it will be within the scope of a skilled person to adjust the paper-manufacturing process, including the raw and auxiliary materials to be used, depending on the wishes of the customer/user and the conditions.

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These above-mentioned flour-processing methods generally and mainly bring the protein fraction into solution, while the starch is solubilized and degraded. The treatment of the flour can be carried out batchwise as well as continuously-in-line.

The invention further relates to a method for manufacturing paper or cardboard, comprising at least a step wherein proteins and starch, i.e. the product as it is recovered from a natural product as unseparated vegetable protein/starch mixture, optionally after being subjected to the above-elaborated treatment analogously with the treatment carried out with native starch, is introduced into the paper fiber matrix.

In conventional paper-manufacturing processes the first treatment consists in so-called pulping - preparing pulp by suspending fiber materials in paper that may or may not have been circulated. In a large vat, by the use of mechanical energy, usually by stirring, and heating, usually with steam or warm water, fiber material is added to water. Through the mechanical and physical treatment, the fiber material is dissolved or dispersed to create a liquid mash, the pulp.

Next, the pulp is subjected to a number of treatments. For instance, the pulp is cleaned, with unusable, nonfibrous material being removed from the pulp. Moreover, if necessary,

a fiber treatment, such a grinding, is carried out. Finally, the pulp is presented in a specific concentration to the paper machine which manufactures paper from the pulp.

In accordance with the invention, during the method for manufacturing paper, at least a step is carried out whereby proteins and starch are jointly introduced into the paper fiber matrix.

During the process pass from pulp vat to paper machine, auxiliary substances, including the protein-starch mixture used according to the present invention, preferably wheat flour, can be added. Moreover, after sheet formation, the protein and starch material can be provided thereon and then -by performing specific treatments - introduced into the fiber matrix.

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For instance, during the paper sheet formation, protein-starch solutions can be introduced into the paper layer or between different paper layers, if any, for instance through spraying or foaming. Also, the protein-starch material can be introduced into the fiber mass by means of a surface treatment or impregnation of the paper already formed, for instance and preferably by means of a size press treatment. Finally, reference is made to the possibility of applying protein material to the dry paper web through spraying or other known application techniques.

In a preferred embodiment of the method according to the invention, protein-starch mixtures are introduced into the paper by means of a size press treatment. During the size press treatment - a treatment which is generally used in the paper industry and is therefore known to a skilled person - a solution or suspension containing the protein-starch mixture to be used is pressed into the paper by means of rolling. The size press treatment can be carried out single-sidedly on the top or bottom side of the paper web, as well as double-sidedly.

In particular for use in the size press, higher protein and starch concentrations have advantages with regard to the

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maximally feasible properties and reduced drying energy thus required.

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In the above-mentioned techniques, it is always important that at least a part of the proteins and the starch be brought into close contact with the fibers in the paper fiber matrix.

Further, it is possible to introduce, in addition to the joint introduction of a protein/starch mixture, supplementary amounts of starch or protein. This can take place at the same place by the use of the same technique, but also at other places in the paper-preparing process.

The invention relates to the use of flour components in the fiber matrix of paper for improving and directing paper properties such as strength, stiffness, permeability, surface properties and elasticity. Moreover, the flour fraction treated according to the invention can be used as glue for fixing the corrugations in corrugated cardboard.

The invention also relates to the use of protein- and starch-containing materials wherein, for attaining the desired paper properties, only the starch fraction is modified chemically or enzymatically. If the starting material contains, in addition to starch, for instance water-soluble proteins, it is not necessary to modify these proteins in order to produce a size having good processing and reinforcing properties. An example hereof is pea meal of which the proteins are soluble in an alkaline medium.

Moreover, for reinforcing the paper, it is possible to use only the starch fraction of starch- and protein-containing materials. On the one hand, this can be effected on account of the fact that the protein, without modification, is water-soluble so that it is either pressed through the paper during the paper treatment, or, present in the paper matrix, does not contribute to the paper properties. On the other hand, the protein can be modified too far, as a consequence of which it does not contribute to the paper properties either. In the most extreme case, the protein is degraded into amino acids. An advantage hereof is that no sharply delimited processing

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degree of the protein has to be set, so that the conversion of starch- and protein-containing material into the suitable size is not a very critical process.

Finally, the invention relates to a method for 5 manufacturing paper wherein vegetable material having as main components protein and starch, preferably grain, is completely processed, comprising separating the vegetable material into (a) a fraction substantially consisting of the cellulose material and (b) a fraction substantially consisting of the 10 protein and starch material, feeding fraction (a) to the usual starting paper fiber mass, for instance during the preparation of pulp, and feeding fraction (b) in the step wherein fiberreinforcing additives are introduced. The fraction fed in the step wherein fiber-reinforced additives are introduced is 15 treated in conformity with the above-described method. In particular, in this aspect of the invention it is possible to completely grind up a vegetable protein and starch source. for instance wheat, and to use the ground-up product directly - after a modification that is analogous with native starch and optionally after a modification wherein the protein 20 properties are optimized - as fiber-reinforcing, qualityimproving component, and to use the residual products, such as the chaff, directly as fiber material. The modification of the flour can consist of a thermochemical conversion, for instance 25 with APS and/or acid, for instance citric acid, optionally in combination with an enzymatic modification with, for instance, amylase and/or protease.

Presently, the invention will be specified with reference to the following examples.

Example 1

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In this example, the effect of the use of flour (IJsvogel-flour, Meneba Nederland; moisture content 13.5%; about 10 wt.% gluten and about 89.5 wt.% starch calculated on the dry product) was studied. For that purpose, suspensions of flour and - for comparison - native starch were introduced into paper by means of the size press method.

The solutions of the above-mentioned macromolecules were set at a desired viscosity by subjecting both the starch fraction and the flour fraction to a degradation with ammonium persulfate (95°C). For an interference-free size press application, the viscosity of the starch suspension should be between 30 and 80 cP; good results with the flour suspension are already obtained at a viscosity of only 15 cP.

The macromolecules-containing solutions were introduced into paper (recycled paper; D-Liner; Roermond Papier) by means of a laboratory size press (Einlehner, rate 30 m/min, temperature 70°C, pressure 2 bar).

The SCT-value and the burst factor were determined according to standardized requirements.

The SCT-value is the maximum compression force per width unit that a test strip can undergo under defined conditions until this strip becomes upset. In this example, the SCT-determination was carried out perpendicularly to the machine direction of the paper. The SCT-value is expressed in kN/m.

The burst factor is determined from a burst pressure measurement. The burst pressure is the pressure exerted on a piece of paper at the moment when the paper cracks. The burst factor (expressed in kPa) is equal to the burst pressure multiplied by 100 divided by the basic weight (g/m^2) .

The results are stated in the following table.

TABLE 1 Increase of the SCT-value and the burst factor relative to the control during the use of flour or starch.

	SCT-value (kN/m)	burst factor (kPa)
starch	0.75	48
flour	0.65	42

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It has been found that the use of flour gives almost the same increase in SCT-value and burst factor as starch. Moreover, a further influencing of the strength properties can be obtained by using a flour suspension having a different viscosity.

Example 2: pretreatments of flour slurries

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- A) treatment with neutral APS
 A suspension of 694 g IJsvogel-flour in 1306 g water (50°C)
 was stirred in a beaker. 2.16 g APS was added, followed by
 stirring for another 30 minutes at 50°C. The resulting
 solution was diluted to a 10 wt.% solution. Heating at 75°C
 took place for 30 minutes, after which the whole was boiled
 for another 60 minutes in a water bath.
- B) treatment with acid APS
 A suspension of 232 g IJsvogel-flour in 1309 g water was
 stirred in a beaker. Citric acid was added to a pH of 4, after
 which 0.72 g APS was fed. After that, the mixture was allowed
 to boil for 60 minutes in a water bath.
- C) treatment with APS and protease
 A suspension of 694 g IJsvogel-flour in 1306 g water (50°C)
 was stirred in a beaker. 1000 μl Neutrase (NovoNordisk) was
 added, followed by stirring for another 30 minutes at 50°C.
 The resulting solution was diluted into a 10 wt.% solution.

 25 2.16 g APS was added. The whole was boiled for 60 minutes in a
 water bath.
 - D) treatment with amylase and protease A suspension of 694 g IJsvogel-flour in 1306 g water (50°C) was stirred in a beaker. 933 μ l Ban α -amylase and 1000 μ l Neutrase (both NovoNordisk) were added, followed by stirring for another 30 minutes at 50°C. The resulting solution was diluted to a 10 wt.% solution. For 30 minutes the temperature was increased to 75°C. After that, the whole was boiled in a water bath for another 30 minutes.
 - Of the four slurries A-D treated, the Brookfield viscosity was determined in cP. The measuring results are shown in the following table.

TABLE 2

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		Brookfield viscosity (cP)
A APS	_	700
B APS	citric acid	40
C APS	protease	40
D α-amylase	protease	25

The flour solutions having viscosities lower than 100 cP could readily be processed on the size press.

Example 3

With a flour slurry obtained according to method D in Example 2 and a 10 wt.% standard starch slurry, test sheets (Testliner 3 Roermond Papier, 160 x 100 mm) were treated on a laboratory size press (Einlewner, rate 30 m/min, temperature 70°C, pressure 2 bar). The impregnated sheets were dried on a drying cylinder at 130°C.

Of these test sheets, the paper properties were determined under conditioned circumstances (23°C, 50% RV) according to standardized methods. The measuring data are stated in the following table.

TABLE 3: Strength and stiffness properties

5	paper property	starch (standard)	flour (enzymatic)	activity rel. to 100% starch
,	take-up (%)	3.2	3.2	
10	burst factor (kPa)	241	273	+13%
	breaking length (m)	6454	6915	+7%
	stretch (%)	1.93	2.13	+10%
	SCT (140 g) (kN/m)	2.46	2.76	+12%
15	stiffness (kNm)	1022	1036	+1%
	CMT 30 (140 g) N	278	284	+2%

In this table, "take-up" is the weight percentage flour/starch relative to the dry paper.

Example 4 Use of pea meal.

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The proteins in pea meal are water-soluble. From pea meal, a flour size is made by modifying only the starch. In a number of experiments, the starch in pea meal is degraded by means of APS or enzymes.

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TABLE 4

5	treatment	size viscosity	SCT-value (kN/m)		
		(cP)			
	ADC	150	not determined		
	APS				
	APS + citric				
	acid	30	4.2		
			4.2		
10	BAN	80			
	Termamyl	60	4.4		

If a suspension of pea meal is only treated with APS, the suspension obtains a high viscosity, as a consequence of which the size is difficult to apply to paper. By reducing the pH of the suspension with citric acid, the APS becomes more effective, so that a size is obtained that does meet the rheological requirements. When this size is applied to paper, the SCT-value is increased. Also the enzyme BAN and Termamyl degrade the starch sufficiently in a suspension of pea meal to obtain a viscosity lower than 100 cP. During application to paper, the SCT-value is increased.

Example 5: test on production scale

In a test reactor, a four slurry with enzymes

(Neutrase) was suspended. Next, this slurry was
thermochemically gelatinized with ammonium persulfate over a
jet-cooker (NEMO-converter). On the paper machine 1 (PM1) of
Roermond Papier, the flour slurry was processed on the size
press.

In particular, a practical production run of the quality Testliner 3 (RP-Maasliner) in 140 g was carried out.

Machine conditions: standard, i.e.:

- 35 composition of raw material according to formulation (recycled material);
 - 2-layer embodiment;

- in-line treatment on size press;
- weight increase though size press treatment: about 3%;
- rate PM: 625 m/min;

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- final moisture content paper: 7%.

During this paper production, the size press solution of native wheat starch (thermochemical conversion with ammonium persulfate (APS)) was replaced during the run by flour (IJsvogel; conversion: starch thermochemically with APS and protein part enzymatically by means of Neutrase).

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Processing: good. Result comparable with 100% starch.

Paper properties: the paper properties are equal to/comparable with starch.

Depositions and foam formation resulting from gluten were not observed in the system.

TABLE 5: Practical test Maasliner (T.L.3), RP-PM1:

20 Г				Flour
	Paper properties		Starch (standard)	FIOUL
·	Gram weight	g/m ²	140.1	139.9
	Final moist. cont	. %	7.1	7.0
25	Take-up			
	(size press)	8	3.2	3.1
	Burst pressure	kPa	340	335
	Burst factor	kPa	243	239
	Breaking 1. m.d.	m	6,610	6,640
30	Stretch m.d.	8	1.90	1.90
	R.C.T. t.d.	kN/m	1.23	1.18
	S.C.T. m.d.	kN/m	4.53	4.65
	S.C.T. t.d		2.30	2.49
	Stiffness m.d	1	960	940
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TABLE 6: properties stated

5		Paper property	Unit	Standard
·	1.	Gram weight	g/m²	ISO 536
	2.	Moisture content	8	ISO 287
	3.	Burst pressure	kPa	ISO 2758
10	4.	Burst factor	kPa	ISO 2758
		$(=\frac{\text{burst pr. x 100}}{g/m^2})$		
	10.	S.C.T.	kN/m	DIN 54518
15	11.	R.C.T.	kN/m	DIN 53134
	12.	C.M.T30	N	ISO 7263
20	13.	Porosity (acc. to Bendtsen)	ml/min	ISO 5636/3
	8.	Stiffness	kN/m	ISO 1924/2
	5.	Tensile strength	kN/m	ISO 1924/2
	9.	Tearing strength	mN	ISO 1974
	14.	Ply-bond (Scott-Bond)	J/m²	Tappi UM 403
	7.	Stretch	8	ISO 1924/2
25	6.	Breaking length	km	ISO 1924/2
	L			

Note: the determinations according to 5,6,7,8,9,10,11 and 12 can be performed in the fiber direction of the paper = machine direction (m.d.) or longitudinal direction (l.d.), or in the transverse direction (t.d.).

Example 6

Example 5 was repeated, the flour slurry with citric acid being suspended. The results were comparable with those in Example 5.

CLAIMS

- 1. Paper or cardboard comprising the components of flour in the paper fiber matrix.
- 2. Paper or cardboard according to claim 1, comprising 0.1-8 wt.% starch and 0.3-2.4 wt.% protein in the paper fiber matrix, calculated on the weight of the dry substance.
- 3. Paper or cardboard according to claim 1 or 2, comprising 2-5 wt.% starch 0.2-1 wt.% protein in the paper fiber matrix.
- 4. Paper or cardboard according to any one of the
 10 preceding claims, wherein the components originate from
 agricultural products, for instance pulses and grains such as
 pea meal and wheat flour.

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- 5. A method for manufacturing paper or cardboard, wherein at least flour is subjected to a treatment known in the paper industry for native starch, after which the treated components of flour are jointly introduced into the paper fiber matrix in one step.
- 6. A method according to claim 5, wherein the flour is treated with a chemical and/or enzymatic starch chain-degrading agent and is then introduced into the paper fiber matrix utilizing a size press.
- 7. A method according to claim 6, wherein the protein fraction of the flour is rendered water-soluble.
- 8. A method for manufacturing paper, wherein vegetable
 25 material of a high protein and starch content, preferably
 grain, is processed completely, comprising separating the
 vegetable material into (a) a fraction substantially
 consisting of the cellulose material and (b) a fraction
 substantially consisting of the protein and starch material,
 30 feeding fraction (a) to the usual fiber mass, and feeding the

fraction (b) according to any one of claims 5-7 in a step wherein fiber-reinforcing additives are introduced.

- 9. Use of unseparated flour components in the fiber matrix of paper or cardboard for improving or adjusting the strength properties, stiffness properties, permeability, surface properties and elasticity of the paper.
- 10. Use of unseparated flour components as glue for fixing the corrugations in corrugated cardboard.